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Response of Crude Oil Slicks to Dispersant Treatment at Sea, 1978 Tests

JBF Scientific Corp., Wilmington, MA

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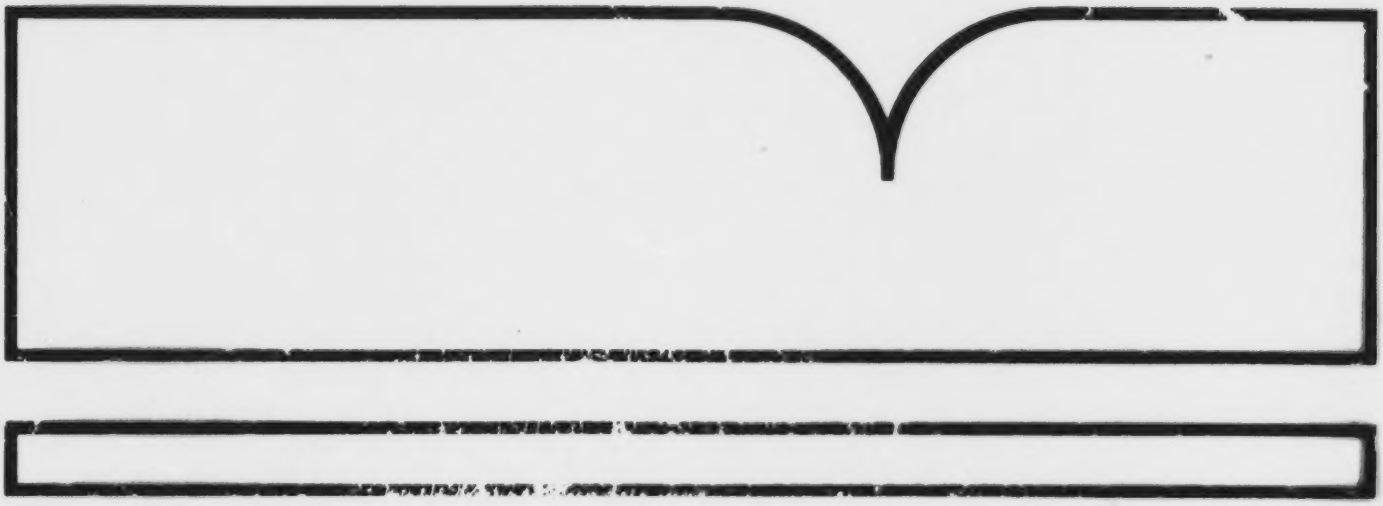

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FINAL REPORT

RESPONSE OF CRUDE OIL SLICKS TO DISPERSANT TREATMENT AT SEA:

1978 TESTS

by

JBF Scientific Corporation
Wilmington, Massachusetts 01887

Grant No. R806056

Project Officer

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This study was conducted
in cooperation with
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Washington, D.C. 20037

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16. ABSTRACT

Four small research oil spills (3.54 m^3 each) were made to compare the physical and chemical behavior of crude oils on the sea with and without dispersant treatment. Work was performed 90 km southeast of New York Harbor under a research ocean dumping permit from the U.S. Environmental Protection Agency (EPA). Each spill was made from a research vessel and was tracked by vessel and aircraft for several hr. Two crude oils were used; one spill of each was treated with dispersant after 30 min, and one was allowed to weather naturally as an experimental control. A self-mix dispersant was sprayed on the two treated slicks from a helicopter that had been fitted with a spray system delivering droplets whose mean diameter was approximately 2 mm. More than 750 samples of background water, water under the slicks, and surface water were taken for chemical analysis. Sampling continued for 6 to 7 hr after each spill. Aerial photographs were taken, and representative photographs are presented in this report. Currents and winds were measured, leading to interpretation of physical transport of the oils. This report complements earlier work performed in 1975 and 1978.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report describes field tests in which a chemical dispersant was applied to controlled oil spills. The findings will assist in predicting the effects of dispersant use.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

Four small research oil spills (1.67 m^3 (440 gal) each) were made to determine the physical and chemical behavior of crude oil slicks on the sea after treatment with a dispersant. Work was performed offshore New Jersey under a research ocean dumping permit from the U.S. Environmental Protection Agency. Each spill was made from a research vessel and was then tracked by vessel and aircraft for several hr. Two crude oils were used; one spill of each oil was treated with dispersant immediately, and one after 2 hr. A self-mix dispersant was sprayed on each spill from a helicopter that had been fitted with a spray system delivering droplets whose mean diameter was approximately 1 mm. More than 1000 samples of background water, water under the slicks, and of the surface water were taken with time for chemical analysis. Aerial photographs were also taken, and representative photographs are presented in this report. Currents and winds were measured, so that physical transport of the oil could be interpreted.

Chemical analyses and visual observations showed immediate treatment to be much more effective than dispersant treatment after 2 hr. Factors contributing to this varying effectiveness include weathering of the oil and the higher dose rate (dispersant volume per unit area) achieved with immediate treatment. Comparison of the 2 crude oils showed Murban to be more effectively dispersed than La Rosa, with other factors held constant. Murban is lighter and less viscous than La Rosa. Vector analyses relating the oil's movement across the sea surface to the wind and current vectors showed that dispersed oil plumes follow the current. Oil that remains on, or returns to, the sea surface is affected by both wind and current.

This report was submitted in fulfillment of Grant No. R806056 by JBF Scientific Corporation and the American Petroleum Institute under the Sponsorship of the U.S. Environmental Protection Agency. This report covers the period January 1, 1978 to December 1, 1980, and work was completed as of December 1, 1980.

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Many extraordinary efforts were made by API task force members and EPA staff to assist in the successful execution of this study. Clayton McAuliffe of Chevron Oil Field Research Company worked with JBF on many aspects of test design and provided the subsurface sampling system that was used. In addition, he took primary responsibility for preparing a technical paper summarizing the results. The paper is Appendix C of this report, and several of its passages were used for descriptions in the main text of the report.

Within JBF, acknowledgment must be made of Stephen Greene's persistence and problem-solving in accomplishing the work aboard ship. Jaret Johnson was Project Manager and coordinated the sea trials from the air.

SECTION 1

INTRODUCTION

In 1975, the American Petroleum Institute (API) began to sponsor controlled field tests to determine the physical and chemical fate of crude oils spilled at sea. These test programs have been in response to a lack of scientific information regarding several aspects of the behavior of spilled oil under actual conditions in the field. Laboratory work at its best is still only a simulation of field conditions, and much of the field work on spills of opportunity has not achieved its potential because of the difficulty of mounting a scientific response immediately after a spill occurs[1].

The API field program includes the following elements in chronological order:

- Four research spills in the Gulf of Maine in 1975, each followed by aerial photography, navigational tracking, and sampling of water and surface oil. These projects were described in API Publication 4290[2] and in papers by McAuliffe[3], and Johnson, McAuliffe, and Brown[4].

- Several research spills off Southern California in 1978. Some of these were tracked scientifically, as above, and others were subjected to a variety of attempts at skimming or dispersant application[5].

- Four research spills in the outer New York Bight in 1978, each of which was treated with a dispersant. These are the subject of this report.

- Several research spills off Southern California in 1979.

- Four research spills in the outer New York Bight in 1979. These will be the subject of a separate report.

PURPOSE

The 1978 east coast tests were made to determine the physical and chemical behavior of two crude oils spilled at sea, as affected by the application of a dispersant. Independent variables included time of slick weathering before dispersant application and oil type. So that comparisons could be made with the 1975 tests in which no dispersants were applied, the same crude oils were used. In addition, biological tests were performed inside and outside the spill areas by the Virginia Institute of Marine Science (VIMS) and by Dr. David Boyles, British Petroleum Company, Ltd.

SCOPE

This report describes the methods, observations, results, and conclusions of the four research oil spill experiments conducted by JBF Scientific Corporation in the outer New York Bight in 1978. Although JBF closely coordinated its efforts with those of the biological researchers, the biological results and their reporting are outside the scope of this report. All data and interpretations relating to physical and chemical fate are provided here.

SECTION 2

CONCLUSIONS

Average total oil concentrations under the immediately dispersed slicks at 1, 3, 6, and 9 m were, respectively: La Rosa - 0.7, 0.7, 0.3 and 0.2 mg/l; Murban - 3.1, 2.4, 0.5, and 0.4 mg/l. The highest concentrations (30 to 90 min after dispersion) were La Rosa, 3 mg/l at 3 m depth; Murban, 18 mg/l at 1 m depth. Because the dispersant:oil volume ratio for these immediately dispersed slicks was about 1:11, the concentrations of dispersant in the water should be less than 10% of these values.

Maximum oil concentrations for dispersion delayed 2 hr were lower (<1.1 mg/l), and only slightly higher than those found under nondispersed oil (highest concentration for La Rosa was 0.5 mg/l; for Murban, 0.9). The less effective dispersion after delayed treatment reflects less efficient dispersant application for these spills, as well as increased oil viscosities due to weathering.

Dispersant treatment of Murban and La Rosa crude oil slicks within 10 min of spilling the oil yielded several differences relative to slicks that were not treated (in 1975) or treated after 2 hr (in 1978). These differences included very thin surface oils in contrast to the thick, viscous appearance of untreated slicks; comparatively high concentrations of oil in the water column; spreading of thin surface films to larger areas than untreated slicks; and, in the case of Murban crude, a readily visible subsurface oil plume.

Subsurface oil plumes moved with the current, whereas surface oil, whether treated or not, moved as the vector sum of current and 1% to 2% of the wind speed.

Below the immediately treated spills, extractable organics concentrations several times higher than background penetrated at least 9 m below the sea surface. Dilution to concentrations at or near background took place in 2 to 3 hr, however, for these spills of 1.67 m^3(440 gal).

The amounts of oil accounted for in the water samples, although very approximate, show that very little oil (<2.4%) was dispersed by the treatments 2 hr after spillage for both crudes. This low percentage of oil dispersed was probably caused by the spraying of dispersant at a uniform dose per unit area, after the oil had had time to become separated into areas of different thickness. For this reason, most of the area of the slick (thin oil) received most of the dispersant, while most of the oil (in thicker patches at the downwind edge of the slick) received an inadequate amount of dispersant.

Approximately 40% to 70% of the Murban crude, immediately treated, was computed to be in the water column. The amount of La Rosa crude was approximately half as much. Visual observations of the immediately treated Murban spill indicated that almost all of the oil entered the water immediately, but that some of it returned to the surface before samples were taken.

Low-molecular-weight (C_1 to C_{10}) hydrocarbon concentrations under the immediately treated Murban spill were much higher than under the immediately treated La Rosa spill. Spills treated after 2 hr had low concentrations of C_1 - C_{10} hydrocarbons in the water.

SECTION 3

RECOMMENDATIONS

Data from this report should be compared with data from laboratory effectiveness tests. If the laboratory tests are valid and if reliable scaling relationships can be derived, other oils and other dispersants should be tested. Thus a data base could be developed to guide dispersant selection and fate predictions for accidental spills.

The relative importance of several variables affecting dispersant effectiveness should be elucidated. Poor dispersant effectiveness with oil that weathered for two hours in these tests may be caused by the weathering itself or by the homogeneous treatment of a non-homogeneous weathered slick. That is, the thicker oil at the downwind edge of the slicks was treated at the same dose as the thinner oil at the upwind edge.

Because this report will be followed by another on the 1979 New York Bight test series, no other recommendations are made at this time. Issues that remain unresolved after analysis of the 1979 data will be identified and recommended for further study in the report on 1979 tests.

SECTION 4

EXPERIMENTAL METHODS

PARTICIPATING ORGANIZATIONS

After JBF and the API had contracted for this project, the U.S. Environmental Protection Agency's Office of Research and Development (EPA/ORD) became sufficiently interested to participate in funding the project by means of a grant to the API for part of the cost. In addition to the research interest by EPA/ORD, EPA's Region II was involved in the regulatory function of reviewing JBF's application for a research permit under PL92-532, the Marine Protection, Research, and Sanctuaries Act of 1972.

These and other relationships among the administrative and technical participating organizations are outlined in Figure 1. Some of the groups shown in Figure 1 will be discussed later in this section with regard to test methods; other groups' activities are described here.

Research Permit (EPA Region II)

An application for a research permit was submitted to the Surveillance and Analysis Division, Marine Protection Program, of EPA Region II on July 19, 1977. A request for clarification and expansion on 18 issues was sent to JBF by Region II on October 27, 1977. JBF's response, amending the original application, was sent to Region II on December 19, 1977. Permit No. II-MA-143-Research was granted by Region II, after public notice and comment, on June 30, 1978. The permit's effective period was October 1, 1978 through March 31, 1980. JBF's work in both 1978 and 1979 was under this permit.

Remote Sensing (NASA)

The National Aeronautics and Space Administration (NASA) is developing technology to monitor various environmental phenomena, including oil spills, from satellites. Development and testing of the equipment is being performed from aircraft. JBF learned of NASA's desire to monitor planned oil spills, and contacted the NASA Langley Research Center in August 1978 to discuss possible cooperation. Subsequent discussions led to several understandings:

- NASA would deploy up to four aircraft to fly over the 1978 test spills for testing various remote sensing techniques.
- After a detailed coordinating session at NASA's Wallops Flight Center, further questions regarding air safety and potential

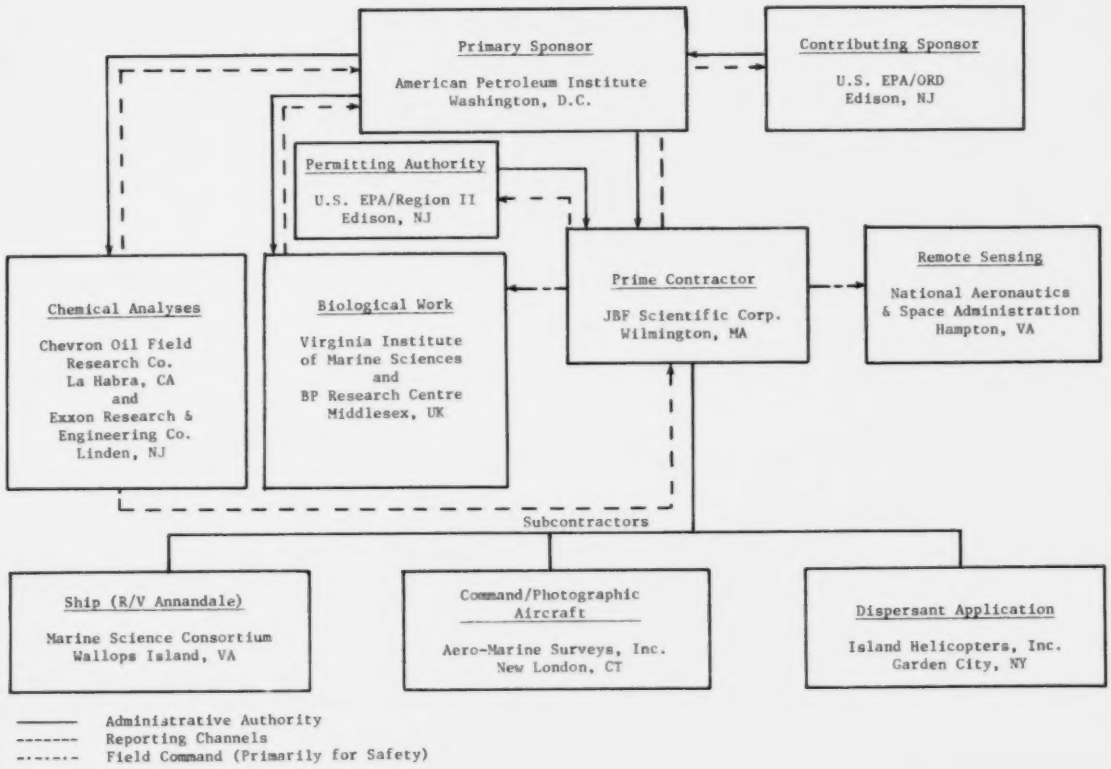


Figure 1. Relationships among participating organizations.

interference with the JBF test mission would be decided by the JBF test director either before or during each test.

- NASA would provide for JBF's use in spilling and sampling, the Research Vessel Annandale, which was under contract to NASA at the time. Coincidentally, JBF had been negotiating with the Marine Science Consortium to lease the Annandale after its NASA contract expired. This cooperative effort enabled JBF to use the Annandale at an early date and without charge, and afforded NASA a unique opportunity to test its remote sensing systems.

SPILL LOCATIONS AND GENERAL CONDITIONS

The area permitted for the tests, and the actual locations of the four test spills, are shown in Figure 2. These sites were selected because their distance from shore and prevailing currents made it unlikely that any oil would approach shore. In addition, all spills were made where the water depth was greater than 40 m to minimize the likelihood of oil contacting resuspended bottom material. Finally, no spills were made when wind was blowing toward shore.

Table 1 shows the general experimental and environmental conditions for the tests. These conditions appear sufficiently similar that weather is not considered a variable affecting test results.

TABLE 1. GENERAL EXPERIMENTAL CONDITIONS

Date	Oil	Time Before Dispersant Application	Wind Speed (m/sec)	Seas (m)	Water Temp. (°C)	Air Temp. (°C)
Nov. 2	Murban	2 hr	4-6	0.3-1	14	15-20
Nov. 3	La Rosa	2 hr	4-6	0.3-1	14	15-20
Nov. 9 (a.m.)	La Rosa	4 min	3-6	0.3-1	13	12-17
Nov. 9 (p.m.)	Murban	5 min	3-6	0.3-1	13	12-17

GENERAL OPERATIONS

Navigation

Both the Annandale and the control aircraft used Loran-C for navigation. Positions were recorded for all sampling stations, for all aerial photographs, and for any other events of significance. The precision of the Loran-C readings is approximately ± 100 ft in the test area.

Current Measurement

Currents were measured by tracking drogues from the ship and from the air. Loran-C positions and times were plotted in the office to derive current vectors. These drogues were of the customary four-vane configuration, presenting a square drag area to the water (1.2 m on a side), with a small staff and flag above the waterline for ease in sighting (Figure 3). The drogues' buoyancy was such that they followed currents approximately 1 to 2 m below the surface.

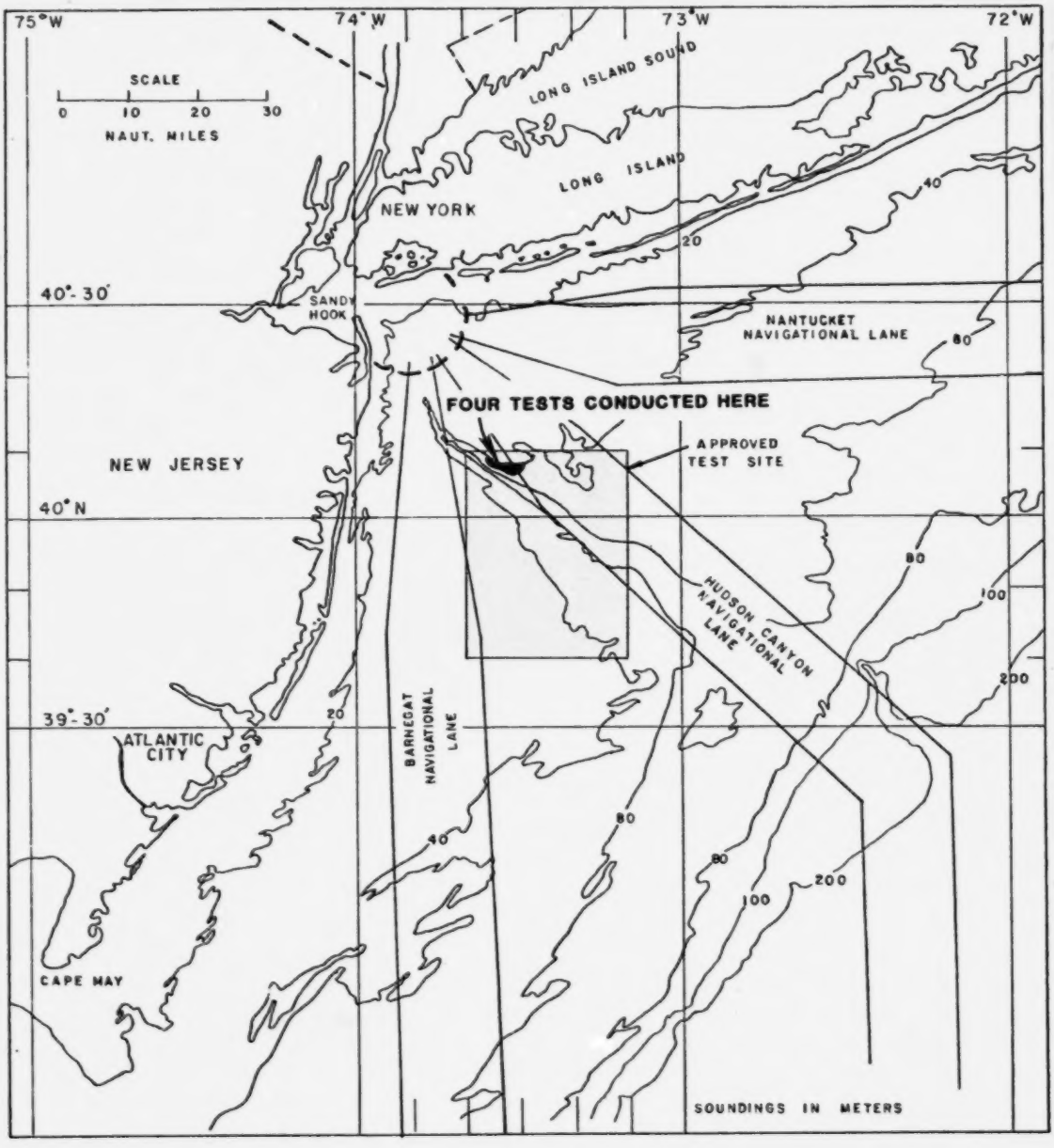


Figure 2. Chart showing test area.

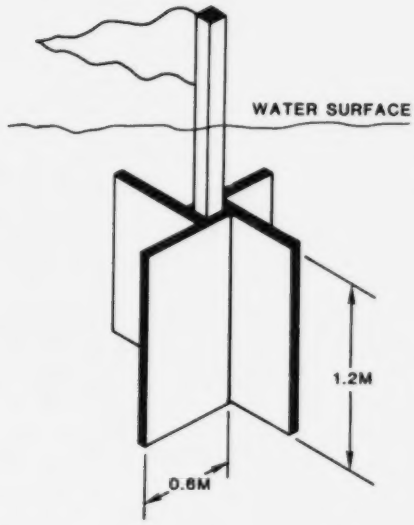


Figure 3. Sketch of four-vane drogue.

Air Control and Photography

The aircraft for operational control and photography was provided by Aero-Marine Surveys, Inc., of New London, CT. A Cessna Model 337G Skymaster was used, carrying the Aero-Marine Surveys pilot and photographer, and the JBF Project Director. The JBF Project Director guided the research vessel to its sampling stations and guided the dispersant-spraying helicopter from this aircraft.

Vertical color photographs were made with two belly-mounted Hasselblad MK-70 mm cameras. Color positive exposures were made on Kodak 11 Color Safety Film and color negative exposures were made on Kodak 8 Color Safety Film. A third camera recorded readings on a data panel for Loran-C position, time, altitude, and heading. All three cameras were activated simultaneously for each exposure. Altitudes for photography varied from 160 to 1300 m.

Spilling Oil

Each spill was 1.67 m^3 (440 gal) of one of the crude oils (Murban from Abu Dhabi and La Rosa from Venezuela). These were the same crudes used in the 1975 test spills that were not dispersed[2].

Each spill was discharged from a 1.9 m^3 tank mounted on the stern of the research vessel through two 7.6 cm diameter hoses. Each hose was 7 m

long, extending over the side to the water surface. The ends of the hoses were on floats, causing the oil to discharge horizontally on the water surface. This minimized both evaporation losses due to discharge above the water, and vertical descent of the oil into the water. The less viscous Murban (0.83 specific gravity, 39° API) discharged in approximately 3 min; the La Rosa (0.91 specific gravity, 23.9° API), in 6 min. All "time after spill" data in this report are based on the beginning of the spill. The research vessel was not moved by its propeller during the spills, but the wind moved the ship and freshly spilled oil slightly. Oil surrounded the stern while the valves were open, but an equiaxed and uniform slick was always in place after the spill was complete and the vessel moved away.

Spraying Dispersant

A self-mix dispersant, suitable for application without added mixing energy (e.g., prop wash or breaker board agitation), was used for all tests.

When dispersant is applied from the air, care is required to produce droplets that are large enough not to drift from the target, but not so large that they plunge through the oil film or do not achieve even coverage of the area. Extensive discussions between JBF and Island Helicopters, Inc. led to a series of dry-land field tests in which various spray nozzles, aircraft altitudes, and flight speeds were checked. Several members of the API Task Force on dispersed oil participated in these field tests. The result was the set of dispersant application specifications listed in Table 2.

TABLE 2. DISPERSANT APPLICATION SPECIFICATIONS

Aircraft:	Bell 206 B Jet Ranger
Spray System:	Belly-mounted Simplex unit with 10-meter boom mounted above skids
Nozzles: Type	Spraying Systems Co. No. D1256 Cone-type teejets
: Number	15
Mean Droplet Diameter:	Approximately 1 mm
Coverage:	Approximately 94 ℓ/hectare (10 gal/acre)

Because the dispersant manufacturer recommended the same coverage, or areal dose rate, regardless of the spill's age, different volumetric dose rates resulted. For the spills dispersed immediately, approximately 152 ℓ (40 gal) were sprayed and the volumetric dose rate was approximately 1:11 (dispersant:oil spilled). For the spills dispersed after 2 hr of spreading and weathering, approximately 360 ℓ (95 gal) were sprayed and the volumetric dose rate was approximately 1:4.6.

For the last three tests, dispersant was discharged while the helicoper flew crosswind in a rapid back-and-forth pattern. In the first test, the helicopter sprayed only while flying upwind, because this was expected to be the most effective method. However, after each downwind leg (not spraying), it was not possible to discern the treated from untreated areas. The pilot then noted that, in a back-and-forth spraying pattern, remnants of the spray could be seen in the air after a fast 180° turn. This pattern was followed for the remaining work.

Another problem with the first test was the pilot's estimation that the slick area was approximately 16 ha (40 acres), meaning that the intended areal dose could not be achieved (the helicopter payload was selected for an expected area of 8 ha and any excess load would have compromised safety). Therefore, only the downwind half of the first slick was treated. Since the downwind portion of an oil slick contains most of the oil[6] this approach should have left only the thin trailing sheen untreated.

SAMPLING AND SAMPLE HANDLING

The sampling program was designed to obtain water samples at approximately equally spaced stations on transects through the surface slicks and emulsion plumes. Figure 4 is a schematic diagram of a typical sample run. Samples on all runs through dispersed or non-dispersed oil were taken at 1- and 3-m depths at all 10 stations, and at 6 and 9 m at Stations 3 and 8. Surface samples were taken, with a small bucket, at all stations during sampling runs through dispersed oil. No surface samples were taken in non-dispersed oil. A sampling run took about 45 min. Between stations, the ship moved at approximately 0.5 m/sec (1 knot).

For the immediately dispersed slicks, the first run was started a few minutes after dispersion, and the second after about 1.3 hr. For the two delayed dispersion tests, one sampling run was made before dispersion (untreated oil), and two after. The two sampling runs after dispersion were immediate and after about 1 hr.

For all of the spills a few samples were also taken 2, 3, and 4 hr after dispersion, at Stations 3 and 8.

The subsurface samples were collected with small submersible pumps with internals of glass-filled polypropylene (Teel Model 1P681). These pumps discharged through polypropylene tubing, at approximately 4 l/min. The pumps were attached approximately 0.5 m below a floating 115-liter (30-gal) steel drum towed 3 m lateral to the bow of the research vessel. In this position, the ship's bow wave did not cause water mixing at the sample inlets. These inlets were 1, 3, 6 and 9 m below the water surface, along a taut vertical line suspending a 23 kg weight from the bottom of the float.

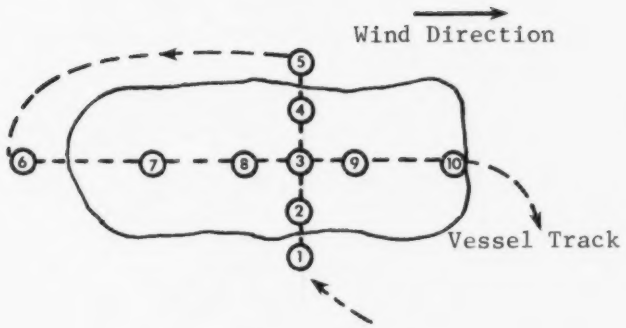


Figure 4. Schematic of immediately dispersed oil slick and location of sample stations for typical 10-station sample run. From McAuliffe, et al. (Appendix C).

The sample gear was lowered and removed from the water outside the observed slicks to avoid surface oil contamination.

Two types of samples were collected at each station and depth: one 1.5-l sample in 1.9-l (0.5-gal) flint glass jug, and duplicate completely filled 300-ml (10-oz) "soft drink" bottles with crown caps. The 1.9-l jugs had been cleaned by rinsing three times with distilled-in-glass carbon tetrachloride (CCl_4) that was checked for purity by infrared (IR) spectroscopy. Immediately after collection, 50 ml of this CCl_4 was added to each jug from an all-glass dispensing pipet. The jugs were sealed with teflon-lined metal screw caps, and hand-shaken for about 10 sec to initiate the solvent extraction of organic matter including the dispersed oil. The CCl_4 also prevented bacterial degradation of the hydrocarbons. In the laboratory, the samples were shaken 2 min to complete the extraction.

Prior to sample collection, about 30 mg of mercuric chloride ($HgCl_2$) was added to each 300 ml bottle to prevent biodegradation prior to analysis. Each bottle was then flushed with reactor-grade helium and sealed with a crown cap (polyvinyl chloride seal). At time of sample collection, each bottle was uncapped, filled to within 3 mm of the top, and resealed with a crown cap. The small air space minimized loss of volatile hydrocarbons to this gas space and possible contamination of sample by hydrocarbons (as well as CCl_4 vapors) that may have been in the atmosphere during sample collection.

Samples of each crude oil were taken from the spill tank in glass bottles with Teflon-lined screw caps.

Chemical Analysis

Total extractable organic matter was measured on the single 50-ml portion of CCl_4, with an IR instrument, as absorbancy at 2930 cm^{-1}. This method measures other CCl_4 soluble compounds such as organic acids, esters, and alcohols in addition to the crude oil. The CCl_4 extracts of a few samples were further analyzed for total nonvolatile (C_{14}+) hydrocarbons, by removing polar organic compounds with a silica gel column and reanalysis by IR. Details of these techniques are given in Reference 7. These analyses were performed by Exxon Research and Engineering Co., Linden, N.J.

Volatile hydrocarbons (C_1 to C_{10} fraction) in the water samples were analyzed by a gas equilibrium method (8) at Chevron Oil Field Research Co., La Habra, CA. Forty ml of Murban and La Rosa oil samples were equilibrated with 140 ml of sea water collected before the oil spills. The oil and water were hand shaken gently and periodically for 24 hr or more. Mercuric chloride added at the time of water collection prevented possible biodegradation of dissolved hydrocarbons during equilibration and prior to analysis. This water was filtered (from one 50-ml glass syringe into a second) to remove any separate-phase oil that may have been dispersed during oil-water mixing. Twenty-five ml of this water was gas equilibrated five times.

These successive analyses were used to measure the equilibrium concentrations of individual C_1 to C_{10} hydrocarbons for the two crude oils, and to calculate individual hydrocarbon distribution coefficients.

The water samples collected at the various stations and depths were then analyzed with a single equilibration using the measured distribution coefficients to calculate concentrations. This gives sufficient accuracy and saves time and cost of multiple equilibrations. For those samples that contained significant separate phase oil, the duplicate sample was filtered and analyzed. Separate-phase oil contributes hydrocarbons to the gas phase in concentrations higher than if the hydrocarbons were only in solution. Method details are given in References 8 and 9.

SECTION 5

RESULTS AND DISCUSSION

PHYSICAL BEHAVIOR

Visual and Photographic Observations

General observations of the spills' physical behavior are discussed here in preparation for the more detailed data presentations and analyses.

Spill 1, Murban Treated After 2 hr--

This spill showed the behavior of Murban as seen in the 1975 test series in the rapid formation of a thick brown water-in-oil emulsion. This material formed a large patch near the downwind edge of the slick (Figure 5). After treatment of this slick with dispersant, the visible appearance of the slick did not change significantly. As described in the previous section, only the downwind half of this slick was treated. An opportunity to compare treated and untreated areas at the same time was thus available. Other than the normally observed differences between upwind and downwind sections, no difference between treated and untreated areas was detectable (Figure 6).

Spill 2, La Rosa Treated After 2 hr--

The downwind, thicker portion of this slick in the untreated condition was dark blue as seen from the air, and quite viscous as seen from shipboard. The overall slick before treatment is shown in Figure 7. Dispersant application produced some immediate, visual changes: in the treated area, iridescence and blue surface oil disappeared, and foam streaks appeared. Within 15 to 20 min after treatment, however, the visual appearance of the slick was similar to its condition before treatment, as shown in Figure 8.

Spill 3, La Rosa Treated Immediately--

No subsurface plume of oil was visible after treatment. The primary difference between this spill's appearance and that of untreated La Rosa slicks was seen from shipboard: the surface oil was thin and transparent, in contrast to the normal opaque, viscous slicks resulting from La Rosa spills. A typical aerial view of this slick is shown in Figure 9.

Spill 4, Murban Treated Immediately--

Dispersant spraying of the freshly spilled Murban caused apparently total entry of the oil into the water as a light brown plume (Figure 10). As time passed, some oil returned to the surface as a thin sheen, and the subsurface plume became diluted and less visible (Figure 11). The subsurface plume after 1 hr was in the upwind part of the area of the surface slick.

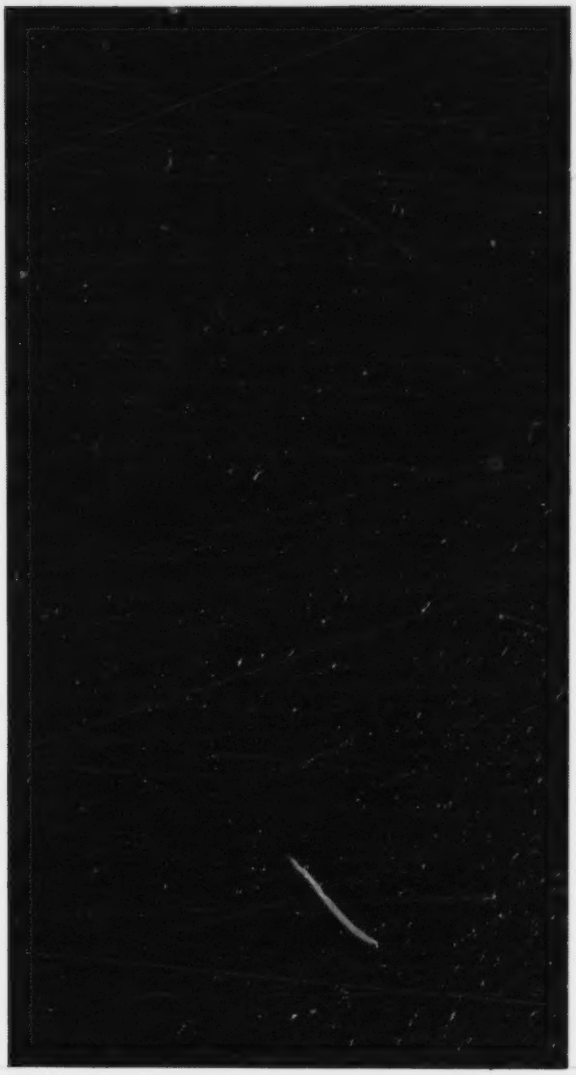


Figure 5. First Murban spill after 53 min, showing water-in-oil emulsion near downwind edge of slick.

Scale: 1 cm = 32 m
Neg. No. 36

Figure 6. First Murban spill after 2 hr and 22 min (22 min after dispersant was sprayed).

Neg. No. 45, 47 and 48
Scale: 1 cm = 36 m

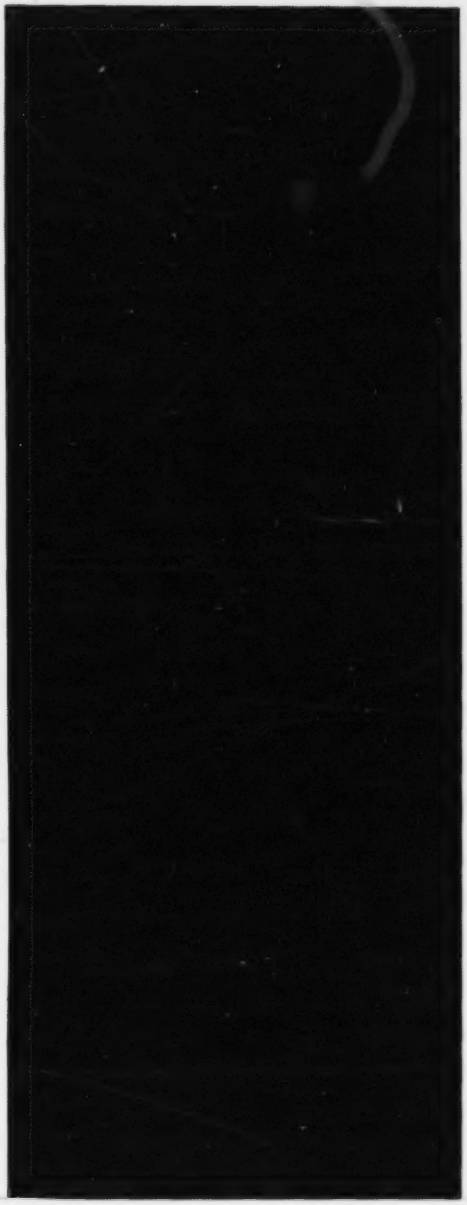


Figure 7. First La Rosa spill after 54 min.

Neg. No. 152
Scale: 1 cm = 32 m

Figure 8. First La Rosa spill after 1 hr and 54 min (20 min after dispersant was sprayed).

Neg. No. 174
Scale: 1 cm = 32 m

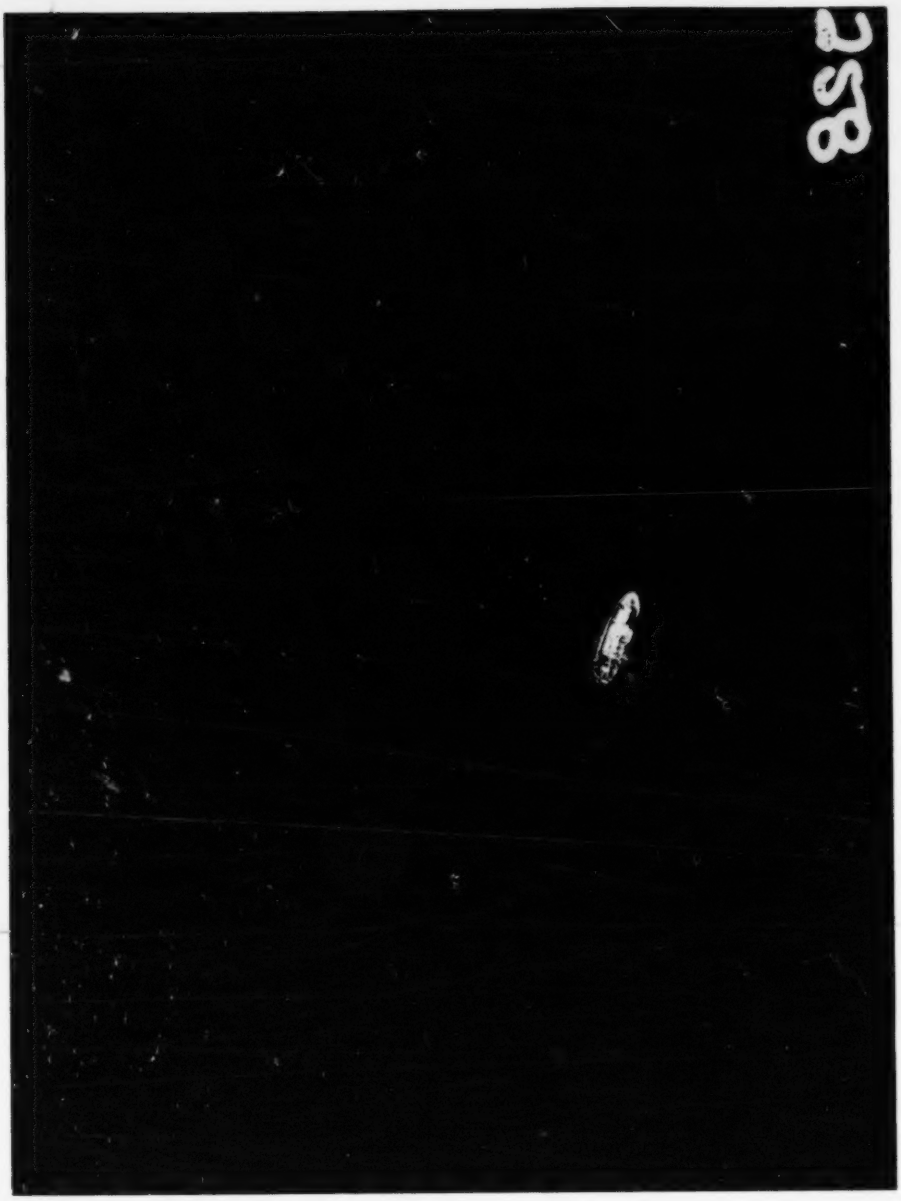


Figure 9. Second La Rosa spill, 32 min after spill (23 min after dispersant spraying began).

Neg. No. 258
Scale: 1 cm = 19 m

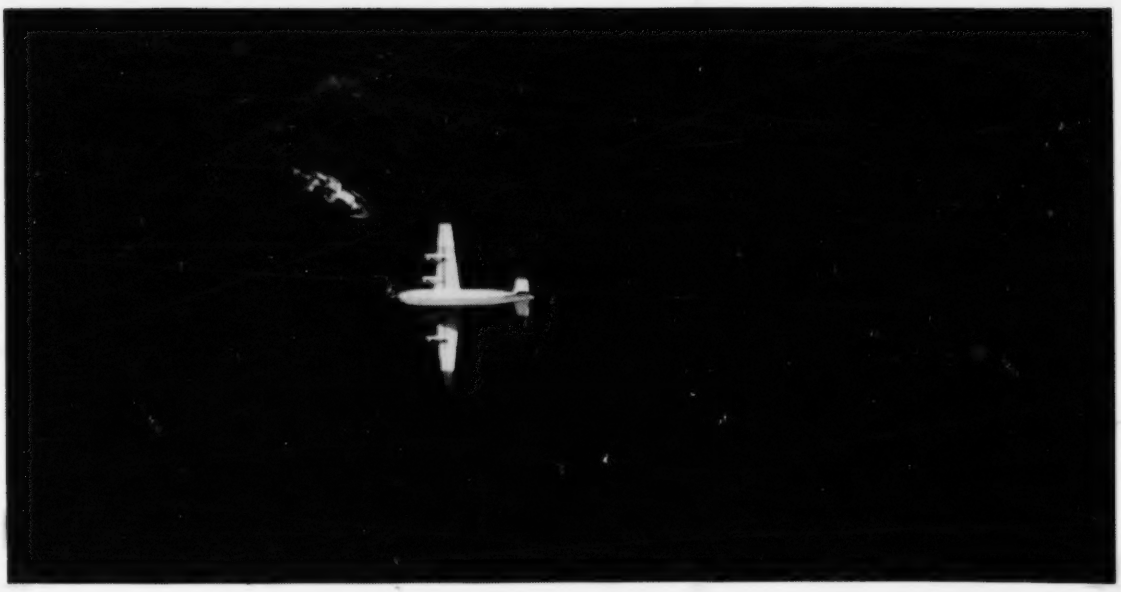


Figure 10. Second Murban spill, 29 min after spill (22 min after dispersant was sprayed).

Neg. No. 338
Scale: 1 cm = 19 m

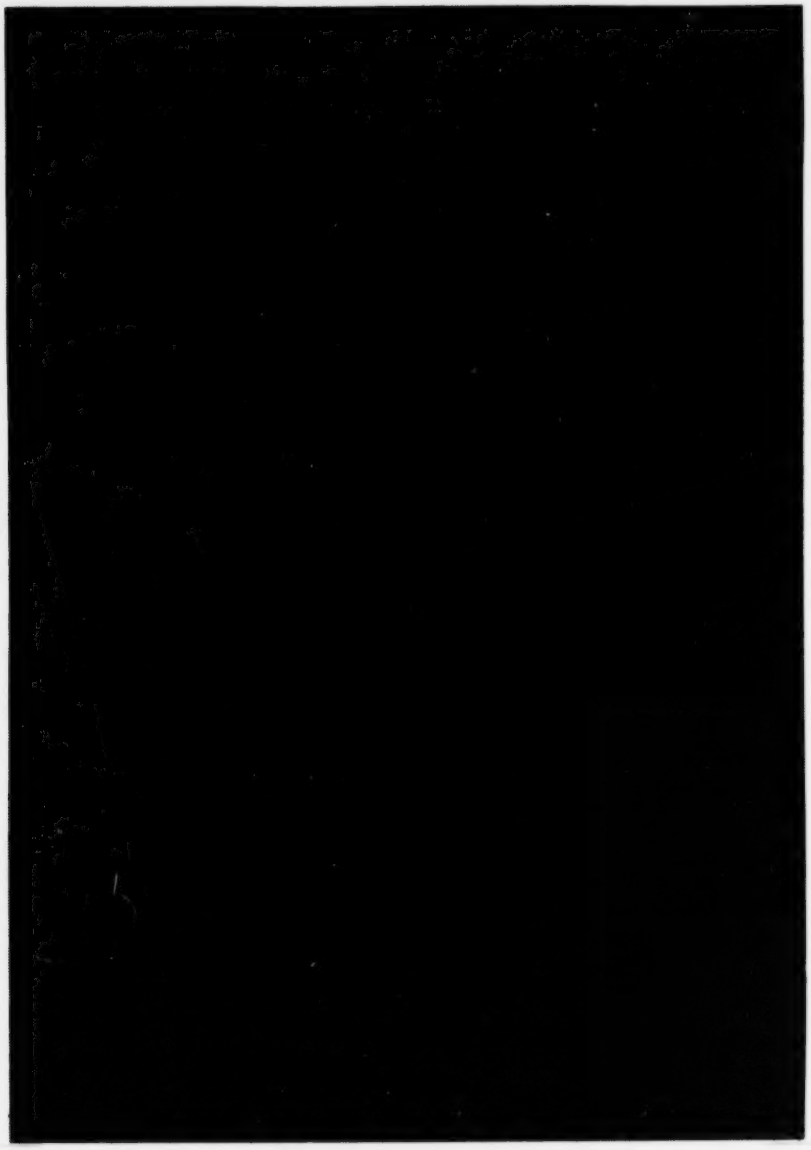


Figure 11. Second Murban spill, 46 min after spill (39 min after dispersant was sprayed).

Neg. No. 342
Scale: 1 cm = 19 m

Slick Spreading

Areas of all four slicks were measured by planimeter techniques on photographs taken at various times. Results for the two La Rosa spills are shown in Figure 12, with 1975 La Rosa data (no dispersant) shown for comparison. Figure 13 shows similar data from the Murban spills of 1975 and 1978.

Several observations can be made, based on these plots and on a review of the aerial photographs.

- The spreading of the 1978 slicks that weathered for 2 hr before treatment was similar to that of the 1975 slicks (untreated).
- The application of dispersant at 2 hr had no apparent effect on spreading rates.
- For the immediately treated La Rosa spill, the spreading rate and area of the slick were both greater than for untreated or delayed-treated La Rosa slicks. To attain such a large area, the slick must have been very thin.
- The immediately dispersed Murban spill spread at a slower rate than untreated Murban slicks for approximately the first 30 min. Ultimately, however, the area of the treated slick became much larger than that of untreated or delayed-treated Murban slicks.

The observed greater spreading tendency of the immediately treated oils is caused, in part, by the reduction in the oil/water interfacial tension achieved by the dispersant. Reduction in viscosity may also contribute. In the case of the Murban spills, the initially slower rate of spreading can be related to the observation that very little oil was on the surface for the first 30 min after dispersant application, as discussed previously. The visible dispersed plume's horizontal rate of spreading below the surface was lower than the rate observed for surface slick spreading with untreated oils. However, as the oil returned to the surface, it formed a slick that spread rapidly into a large, thin sheen.

Slick Drift

Winds and currents affect the transport of oil slicks across the sea surface. The 1975 work confirmed several literature findings in that those spills moved as the vector sum of current and approximately 1% to 3% of the wind vector.

Figures 14 through 17 show the transport of surface oil, as well as wind and current vectors, for the four 1978 spills. During the time of observation for each spill, winds were fairly consistent. Current direction changed on each test day, however. During Spill No. 1 (Figure 14), the current heading changed from ESE to NNE, producing a change in the direction of surface oil transport. Spill No. 2 (Figure 15) showed an even more pronounced shift in current and oil directions. On the third test day,

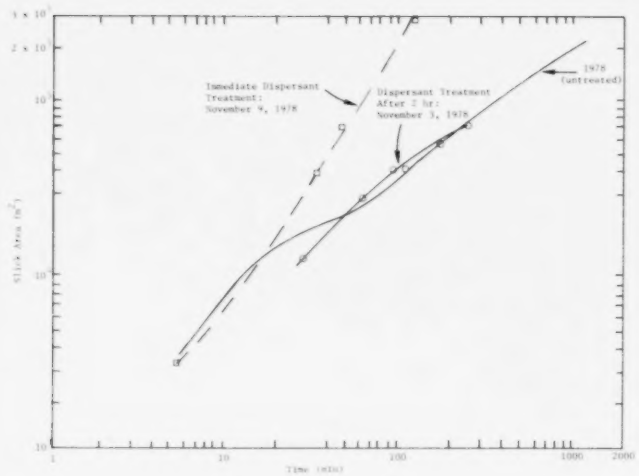


Figure 12. Slick area growth with time, La Rosa spills.

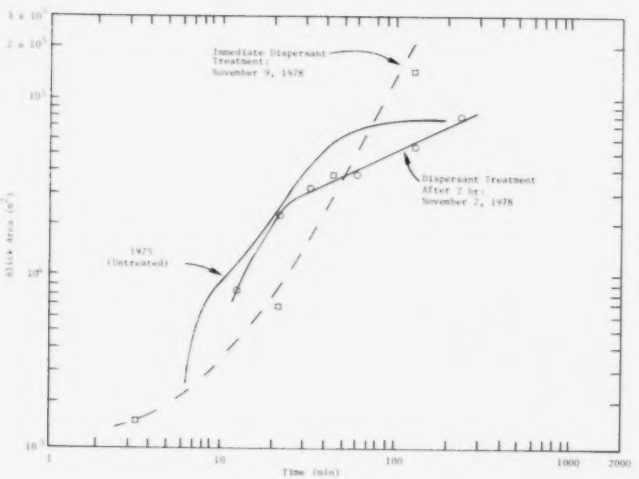
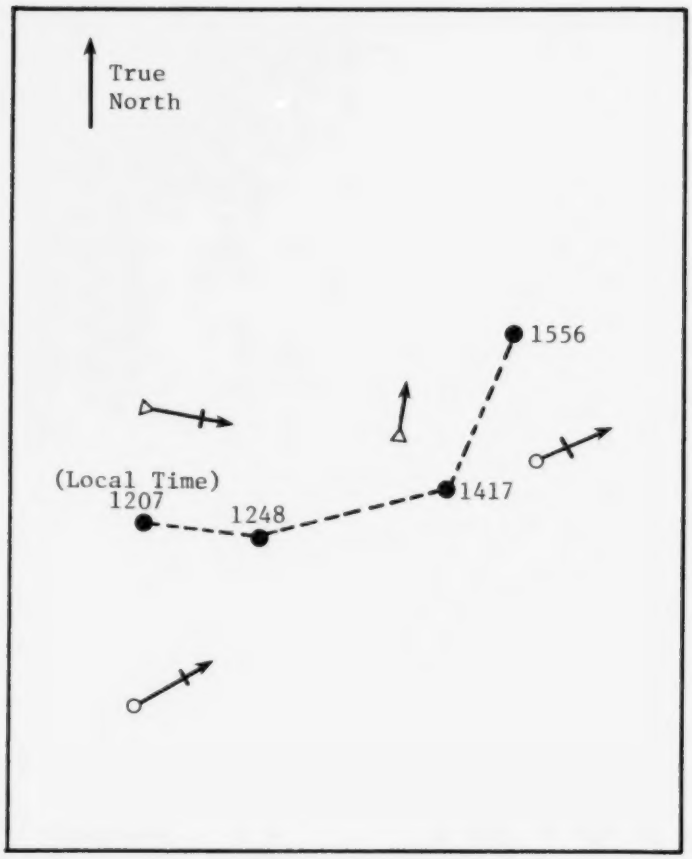


Figure 13. Slick area growth with time, Murban spills.



SCALE:

1853 m
(1 Naut. Mi.)

LEGEND:

Wind Vector

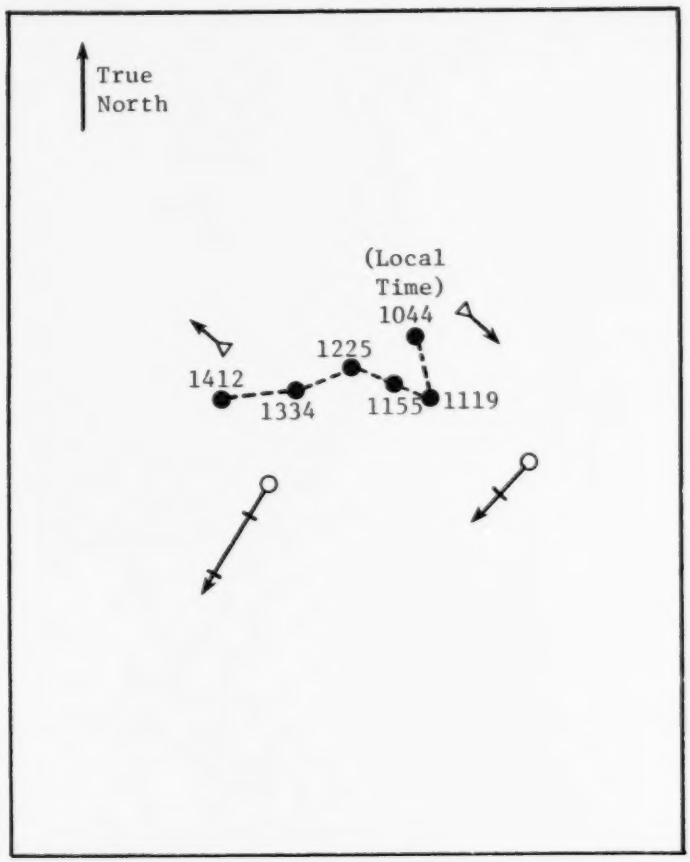
1 segment = 2.6 m/sec (5 knots)

Current Vector

1 segment = 0.13 m/sec (0.25 knots)

Slick position (Leading Edge)

Figure 14. Effect of wind and current on slick position: Spill No. 1, Murban treated after 2 hr.



SCALE:

1853 m
(1 Naut. Mi.)

LEGEND:

Wind Vector

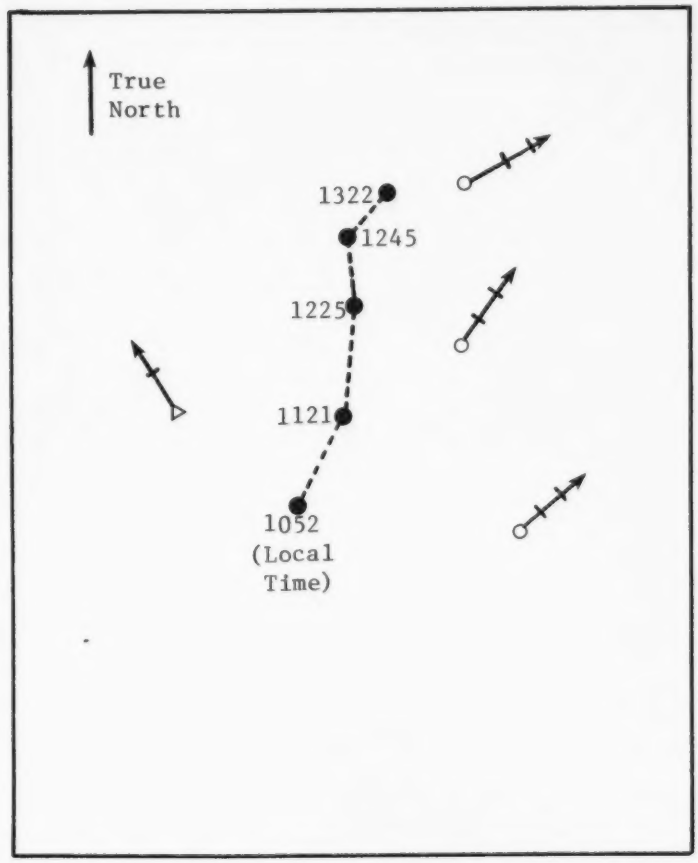
1 segment = 2.6 m/sec (5 knots)

Current Vector

1 segment = 0.13 m/sec (0.25 knots)

Slick Position (Leading Edge)

Figure 15. Effect of wind and current on slick position: Spill No. 2, La Rosa treated after 2 hr.



SCALE:
1853 m
(1 Naut. Mi.)

LEGEND:

Wind Vector

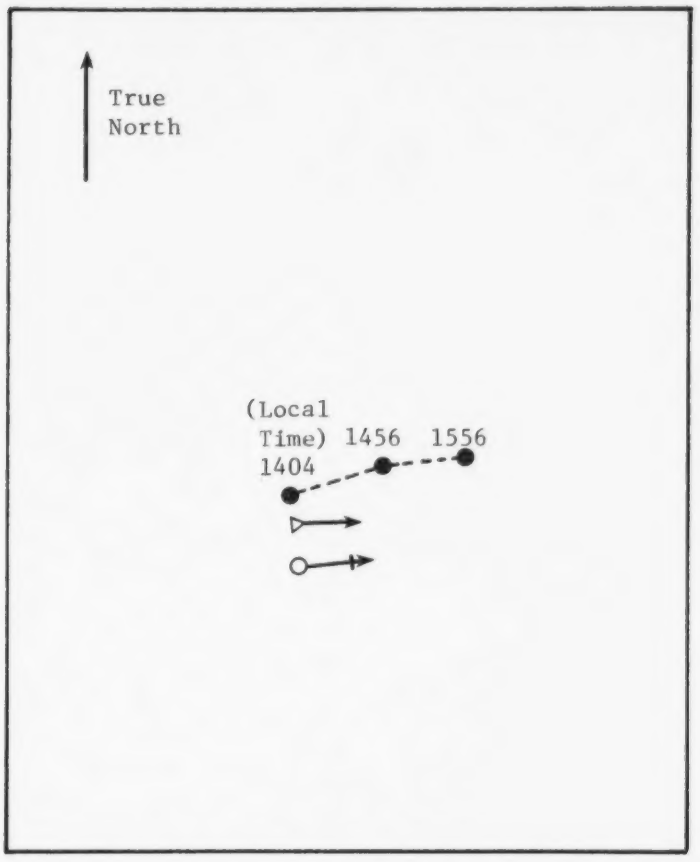
1 segment = 2.6 m/sec (5 knots)

Current Vector

1 segment = 0.13 m/sec (0.25 knots)

Slick Position (Leading Edge)

Figure 16. Effect of wind and current on slick position: Spill No. 3, La Rosa immediately treated.



SCALE:
1853 m
(1 Naut. Mi.)

LEGEND:

Wind Vector

1 segment = 2.6 m/sec (5 knots)

Current Vector

1 segment = 0.13 m/sec (0.25 knots)

Slick Position (Leading Edge)

Figure 17. Effect of wind and current on slick position: Spill No. 4, Murban immediately treated.

which included two test spills, current was consistent during each spill but shifted directions between spills, contributing to the different headings of the surface oils from these spills.

Analysis of the velocity vectors for oil, current, and wind showed results similar to those from the 1975 tests: the effect of the wind on all surface slicks was a vector whose magnitude was 1% to 2% of the wind vector, and roughly parallel to the wind vector. These effects on surface oil movement, summarized in Table 3, were independent of whether the oil had been treated with dispersant. The direction of movement of subsurface oil is discussed later, where the subsurface plume's fate is inferred through chemical analyses for known sample positions.

TABLE 3. COMPARISON OF WIND EFFECT VECTORS WITH WIND VECTORS

Spill	Time Interval	Wind effect compared to wind vector	
		Approximate Heading	Velocity Ratio
Murban - 2 hr	Before treatment	parallel	1%
	After treatment	30° to Right of wind	1%
La Rosa - 2 hr	Before treatment	20° to Right of wind	2%
	After treatment	20° to Left of wind	1%
La Rosa - immed.	After treatment	20° to Right of wind	2%
Murban - immed.	After treatment	parallel	1%

CHEMICAL ANALYSES

Analyses of the water samples provided information that complements the physical observations for overall indications of fate of the oil and some of its specific fractions.

Total Extractable Organics

Analyses of the CCl_4 extracts by infrared spectroscopy were performed by Exxon Research and Engineering Co. (ER & E). ER & E's findings are presented as Appendix A, and the interpretations of those data are developed in this section. As the discussion will show, highest oil concentrations and most interesting patterns were found in the water samples from the spills that were treated immediately. These spills (No's 3 and 4) are therefore discussed first.

The crossed transects of a sampling run permit a three-dimensional analysis of plumes of dispersed oil (i.e., in crossed vertical planes). However, the limited sampling at 6 and 9 m (only at Stations 3 and 8) gives a limited view of dispersion at these depths. The 1975 work (2) showed that these two crude oils dispersed only slightly to depths up to 3 m without dispersant treatment, even in rough seas. In addition, McAuliffe et al. (9) found no oil at 6 m below the sea surface near a platform blowout that was treated with dispersant. Therefore, significant dispersion of oil down to 6 and 9 m was not expected. These depths were added only to verify the earlier results, but the detection of measurable oil at 6 and 9 m in this work was frequent. In subsequent studies conducted in October 1979, all stations were sampled through 9 m, and all samples were analyzed.

La Rosa Spill, Immediately Dispersed--

Figure 18 shows the total extractable organic matter concentrations with depth along the two transects of the first sampling run following the immediate dispersion of La Rosa crude oil. The vertical scale exaggeration is about 45X. The contour for 0.25 ppm was at approximately 9 m at its deepest point; for the 1.0 ppm contour, 4 to 5 m.

The shape of the 2.0 ppm contour on the transect of Stations 6 through 10 is interesting in its asymmetry. Relying as it does on one data point for its asymmetric shape, this might be suspected as an experimental artifact. However, the second set of transects, approximately 1 hr later (Figure 19) produced the same type of contour. An unexplained, but real, hydrodynamic effect appears responsible for this unusually shaped isopleth.

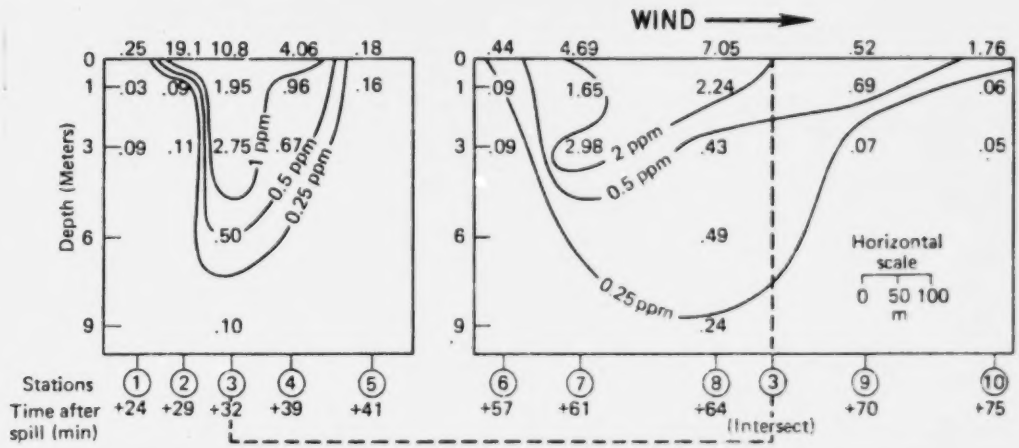


Figure 18. Total extractable organic matter (ppm) in water samples collected during first sample run through La Rosa crude oil spill immediately dispersed (oil spilled 1019, dispersed 1028-1035). Vertical scale exaggeration about 45x. From McAuliffe et al. (Appendix C).

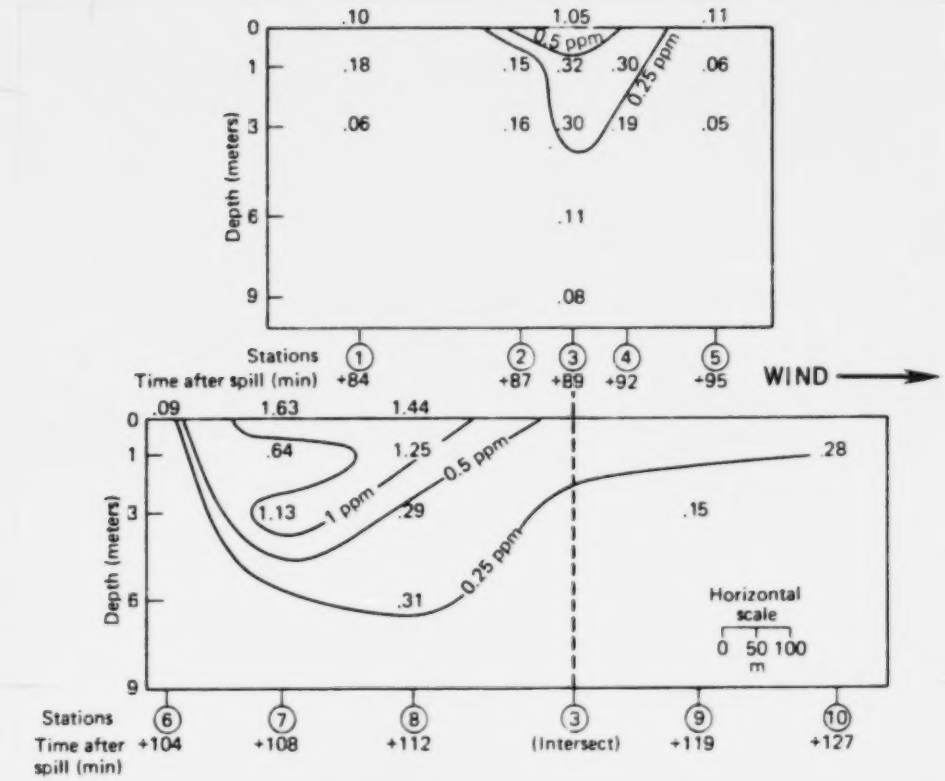


Figure 19. Total extractable organic matter in water samples collected during second sample run through La Rosa crude oil spill immediately dispersed. Vertical scale exaggeration about 45x. From McAuliffe et al. (Appendix C).

Another observation based on Figures 18 and 19 is that the plume of dispersed oil extended much more in the direction parallel to the wind (transect 6 - 10) than in the crosswind direction. In addition, the plume remained beneath the visible surface slick. Figure 16 showed that the current was at approximately 90° from the wind direction during this spill's period of observation (current to the northwest, wind to the northeast). One can postulate that the immediately dispersed subsurface oil should be advected only by the current vector. The oil behavior that should result from this condition is shown schematically in Figure 20. In Figures 18 and 19, subsurface oil was shown to be more heavily concentrated at the upwind end of the slick, indicating that the behavior suggested in Figure 20 did occur.

If the subsurface plume's buoyancy is effectively neutral because of small droplet size, water circulation should cause a large number of droplets to be at the surface at any time. While at the sea surface, droplets may coalesce with residual surface oil or with each other. This phenomenon

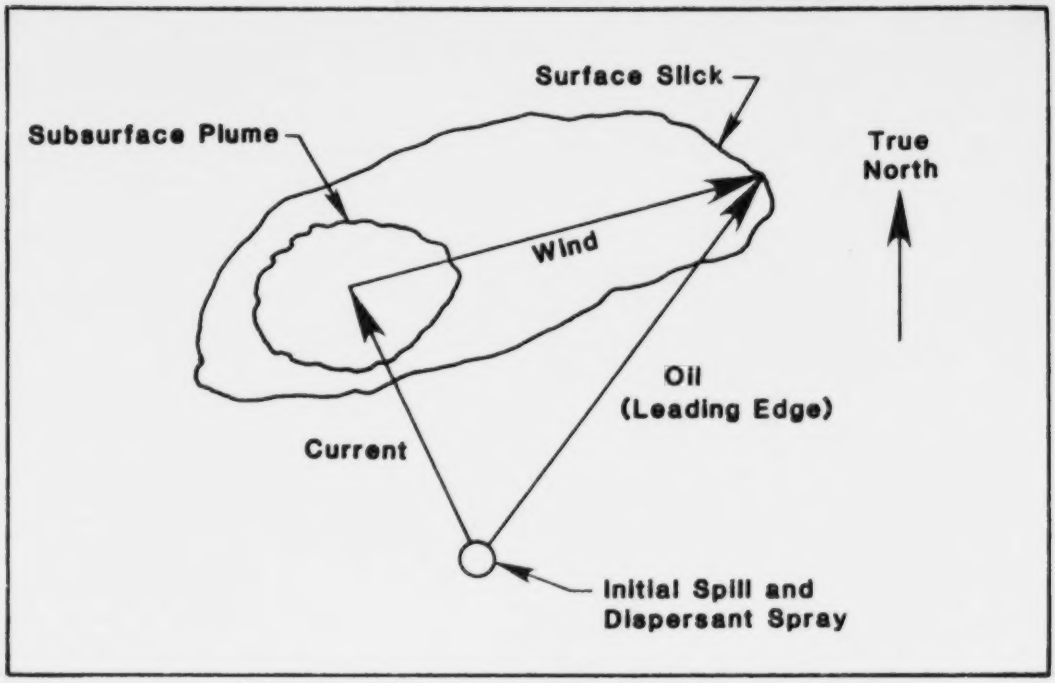


Figure 20. Schematic view of surface slick and subsurface plume's spreading and transport as affected by wind and current.

may be another reason for the observed rapid spreading rates of the immediately dispersed oils. Such a mechanism could cause dispersed plumes to be in contact with thin surface slicks as long as both are detectable. If this hypothesis is correct, an on-scene vector analysis, coupled with visual observation of the surface sheen, may make the tracking of dispersed plumes for extended periods an easy task, even if the subsurface oil cannot be seen.

Comparing Figures 18 and 19 shows the effect of dilution as the subsurface plume dispersed. Another way to view the dilution is shown in Figure 21 for the immediately dispersed La Rosa spill. Concentrations at the center of the plume are plotted with depth over time. Because each depth concentration is a single analysis, great reliance should not be placed on an individual point. As expected, a steady decrease in concentrations toward background values occurred over time.

Murban Spill, Immediately Treated--

The subsurface plume shape for the immediately treated Murban spill is shown for the first sampling transects in Figure 22. Comparison with Figure 18, representing a similar time span for similarly treated La Rosa crude,

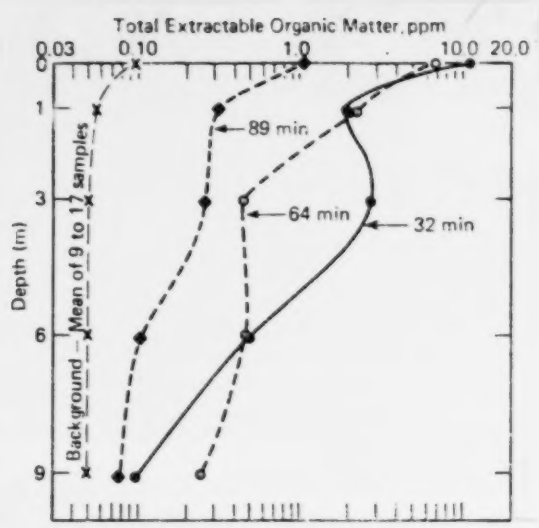


Figure 21. Comparison of concentration - depth profiles at one station for various times under the immediately dispersed La Rosa crude oil spill.

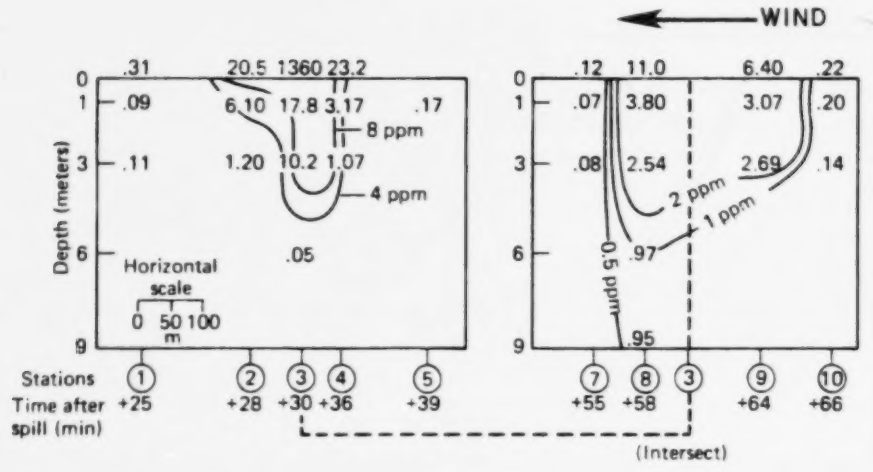


Figure 22. Total extractable organic matter (ppm) in water samples collected during first sample run through immediately dispersed Murban crude oil spill (oil spilled 1404, dispersed 1411-1416). Vertical scale exaggeration about 45x. From McAuliffe et al. (Appendix C).

shows generally higher concentrations for Murban. Dispersed oil was also found in higher concentrations at greater depths (almost 1 mg/l at 9 m).

Figure 23 shows the subsurface plume shape for the second set of transects on this spill. Because only a few samples for the station 1 to 5 transect were analyzed, that transect is poorly characterized. The plume appears centered beneath the surface slick, however. As Figure 17 showed, the wind and current were approximately parallel during this test, so that the subsurface plume and surface oil would be expected to remain together. The dilution of this plume with time, as expected, proceeded similarly to that of the plume from the immediately treated La Rosa spill. Comparison of Figure 24 (Murban) with Figure 21 (La Rosa) shows this similar time pattern.

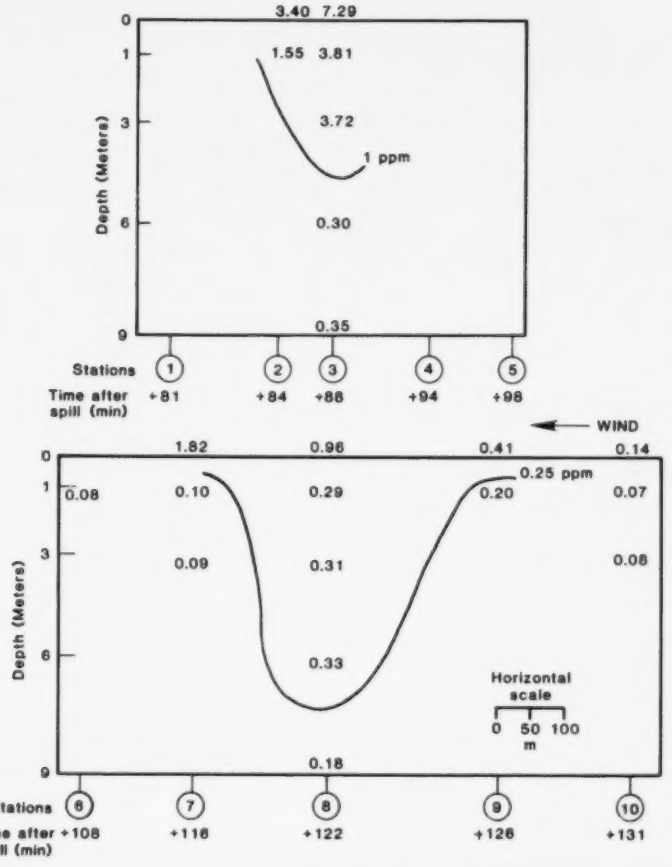


Figure 23. Total extractable organic matter (ppm) in water samples collected during second sample run through immediately treated Murban crude oil spill. Vertical scale exaggeration about 45x.

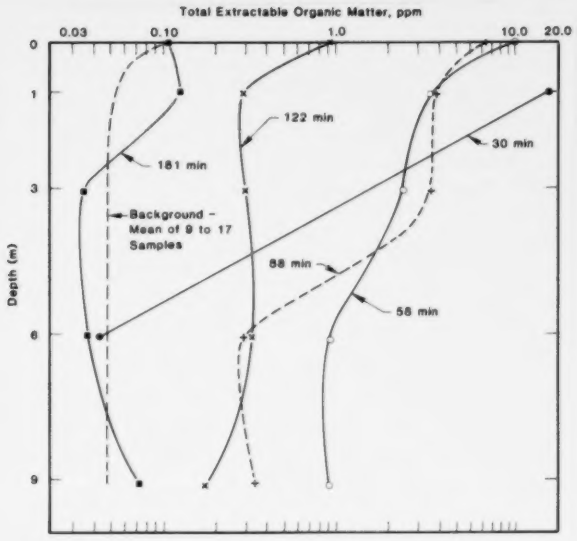


Figure 24. Comparison of concentration-depth profiles at one station for various times under the immediately dispersed Murban crude oil spill.

Spills Treated After Two Hr--

The data for the two spills that were allowed to weather for 2 hr before dispersion do not allow such clear graphical display. Most values for total extractable organic matter were much lower than those from the immediately dispersed spills. One explanation is the larger area to be treated after 2 hr, with a consequently larger water volume available to dilute an equivalent amount of oil.

Another problem is the nonhomogeneity of the oil slicks after 2 hr. Most of the oil was concentrated in the leading (downwind) part of the slick, in perhaps only 10% of the total slick area, as observed by Hollinger and Mennella[6]. The dispersant was applied uniformly over the whole slick rather than concentrated on the area of heavy oil. If a "lens" comprising 10% to 20% of the slick area contained 80% to 90% of the oil, the volumetric application rate of dispersant to the oil in the lens would be approximately 1:25, in contrast to the gross rate of 1:4.6.

Therefore the dispersant to oil volumetric application rate for most of the oil was not as high as for the immediately dispersed spills, which were treated before appreciable spreading had occurred. Weathering also would have increased oil viscosities, and thereby should have decreased dispersant effectiveness.

Comparisons Among Tests--

Extractable Organics Concentrations--Concentration lines for the immediately treated Murban spill (Figures 22 and 23) show higher values than with La Rosa Figures 18 and 19). Dispersed oil was also found in higher concentrations at greater depths (almost 1 ppm at 9 m).

Figure 25 compares concentration-depth profiles of the two crude oils, for samples from the center of the plume at similar times after oil discharge and dispersion. Again, each concentration is a single data point.

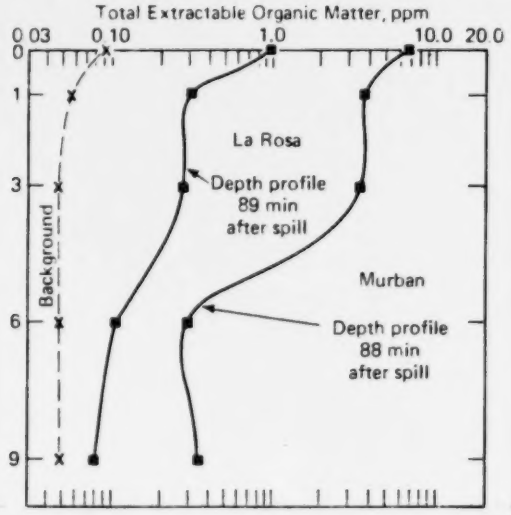


Figure 25. Comparison of concentration - depth profiles for La Rosa and Murban crude oils at about the same time following discharge and dispersion. From McAuliffe et al. (Appendix C).

A summary of the total extractable organic matter in water under the four research oil spills is shown in Table 4. It includes only values exceeding 0.10 ppm (approximately two times background). Untreated oil dispersed naturally in the water to a lesser extent than chemically treated oil. Immediate treatment was more effective than treatment after 2 hr.

The greatest difference between oils was evident when they were dispersed immediately. Murban oil concentrations were higher at all water depths than for La Rosa. The slightly higher concentrations for La Rosa compared with Murban following delayed dispersion may reflect differences in chemical application and/or sampling locations.

Amount of oil accounted for--Computation of the amount of oil in the water was performed with the following procedure and simplifying assumptions:

- For the figures showing reliable isopleths of extractable organics (Figures 18, 19, and 22), the volume inside each isopleth was approximated as an inverted pyramid, bounded by plane surfaces extending from the nadir of the pyramid, near the isopleth lines to the sea surface.

TABLE 4. SUMMARY OF CARBON TETRACHLORIDE EXTRACTABLE ORGANIC MATTER IN WATER FROM UNDER FOUR RESEARCH OIL SPILLS (ppm)*

Sample Description	La Rosa			Murban		
	n**	Maximum	Mean	n**	Maximum	Mean
Not dispersed						
1 m	4	0.22	0.13	1	0.95	-
3 m	3	.51	.26	2	.16	0.14
Dispersed at 2 hr						
1 m	7	.23	.15	8	.18	.13
3 m	7	1.05	.27	4	.11	.10
6 m	2	.65	.38	1	.14	-
9 m	1	.29	-	1	.12	-
Dispersed within 10 min						
1 m	16	2.24	.69	13	17.80	3.10
3 m	14	2.96	.67	9	10.20	2.45
6 m	5	.50	.31	4	1.00	.45
9 m	1	.25	-	4	.95	.40

*Background concentrations (ppm); 1 m, 0.061; 3 m, 0.050; 6 m, 0.048; 9 m, 0.051

**Number of samples

- The volumes of the pyramids thus described were calculated and the amount of extractable organic matter was determined by multiplying by the concentration, with appropriate dimensional conversions.
- Double accounting was avoided by using the incremental volumes and concentrations for each pyramid, and summing the results.

The results should be used with great caution as to absolute quantities of oil in the water, but the relative amounts for different oils and treatments should be useful for comparison because all computations used the same assumptions. The reasons for the approximate nature of the absolute oil quantities include:

- The isopleths are not "snapshots", but represent changes in time as well as position. Therefore average extent (area and volume of each plume during each transect) was roughly approximated.

- The isopleths do not in fact describe pyramids or even cones, but the pyramid shape was selected because of simplicity. Given the amount of judgment used in drawing the isopleths among the sparse data points, a more sophisticated approach to volume computations was not justified.

Results are shown in Table 5.

TABLE 5. APPROXIMATE VOLUME OF EXTRACTABLE ORGANICS ACCOUNTED FOR IN WATER SAMPLES UNDER EACH SPILL

Oil	Time to dispersant Spraying	Approximate Amount oil in water (ℓ)*
Murban	Immediate	680
Murban	2 Hr	40
La Rosa	Immediate	340
La Rosa	2 Hr	40

* Spilled oil volume was 1665 ℓ.

The many judgments and other sources of error leading to these results could possibly cause these values to be off in absolute terms by as much as 50 to 60%. The relative amounts, which are more reliable, clearly show the advantage of applying dispersant to these oils as soon as possible. The relative ease of dispersing Murban crude compared to La Rosa crude is also evident. These relative findings concur with visual observations of effectiveness.

Petroleum Hydrocarbons

Petroleum hydrocarbons (C_{14}+) were determined on three of the extracts. Extractable organic matter was 2.24, 1.25, and 2.54 mg/l; C_{14}+ hydrocarbons were respectively 1.43, 0.72, and 1.97 mg/l. Petroleum hydrocarbons averaged 76% of the total extractable organic matter. This is in the range previously observed (7) for a much larger number of analyses. However, the actual crude oil content of the original CCl_4 extracts is higher because hydrocarbons

<C_{14} are lost when the CCl_4 is evaporated to 1 ml prior to adding to the top of the silica gel column. Thus, the C_{12} and C_{13} with lesser amounts of C_9 to C_{11} hydrocarbons are present in the original CCl_4 extract. This may amount to 10 to 15%, thereby raising the oil content to 85 to 90%. The percent oil may be even higher for those samples with the highest oil content (>5 ppm).

The polar organic compounds removed by silica gel appear to exceed the extractable organic matter from background water samples outside the oil spill areas (particularly noticeable when the extractable organic material ranges from 0.2 to 1 ppm). A possible explanation is that crude oil acts as an organic solvent, extracting and concentrating natural organic compounds in sea water.

Low-Molecular-Weight Hydrocarbons

As described in Section 4, individual hydrocarbons in the C_1 to C_{10} fraction were measured by gas chromatography. The raw data are provided as Appendix B. Interpretation of these data, as developed by Clayton McAuliffe of Chevron Oil Field Research Company, is detailed in Appendix C, pages 8 through 16. A brief summary of the data and findings is presented below.

To compare the two oils, representative data shown in Table 6 can be used.

Review of Table 6 yields the following observations:

- Of all the La Rosa samples from 6 and 9 m, only one showed detectable C_1 to C_{10} hydrocarbons.

- C_1 - C_{10} concentrations under Murban spills were much higher than those under La Rosa spills for similar locations and times. Two factors contribute to this difference: the better dispersion of Murban and the fact that, when fresh crude oil was equilibrated with clean sea water in the laboratory, the C_1 - C_{10} fraction's concentration was nearly twice as high for Murban as for La Rosa.

In addition, review of all the data in Appendix B shows that, although similar numbers of samples were collected from all four spills, the numbers of samples with detectable C_1 - C_{10} hydrocarbons were (not counting duplicate samples):

Murban, 2 hr weathering - 8 (6 before spray, 2 after)
La Rosa, 2 hr weathering - none
Murban, immediate spray - 38
La Rosa, immediate spray - 17

The more effective dispersion of Murban is obvious.

TABLE 6. COMPARISON OF TOTAL LOW-MOLECULAR-WEIGHT HYDROCARBON CONCENTRATIONS FROM STATIONS AT CENTER OF PLUMES, IMMEDIATELY AFTER IMMEDIATELY TREATED SPILLS*

Time after spill (min)	Depth (m)	Oil	Total C_1 - C_{10} hydrocarbons (ppb)
33	0	La Rosa	8.46
30	0	Murban	3693
33	1	La Rosa	2.62
30	1	Murban	72.1
33	3	La Rosa	1.67
30	3	Murban	16.6
33	6	La Rosa	1.22
58	0	Murban	46.2
58	1	Murban	16.5
66	1	La Rosa	3.56
58	3	Murban	24.8
58	6	Murban	4.00
58	9	Murban	3.29
88	0	Murban	25.3
88	1	Murban	25.3
90	1	La Rosa	1.41
88	3	Murban	19.5
88	6	Murban	13.0
88	9	Murban	5.45

*Where no entry appears (e.g., 33 min, 6 m, Murban), C_1 - C_{10} hydrocarbons were less than 0.4 ppb.

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APPENDIX A

ANALYTICAL SUPPORT TO THE API INVESTIGATION OF THE EFFECTIVENESS OF SURFACE-ACTIVE AGENT IN COMBATING OPEN OCEAN SPILLS

R. A. Brown
T. D. Searl*

SUMMARY

Four hundred samples for four planned oil spills were collected and half of them were analyzed for extractable organic content (includes hydrocarbons and higher molecular weight alcohols, esters, and organic acids). A few samples were analyzed for total nonvolatile hydrocarbons. An average value of 0.68 was observed for the ratio nonvolatile hydrocarbons/extractable organics.

INTRODUCTION

In November 1978 the JBF Scientific Corporation conducted a series of four planned oil spills for the API in the Atlantic Ocean about 30 miles off the New Jersey coast. These spills were to investigate the effectiveness of a surface-active agent in combating open ocean spills. The role of the Analytical and Information Division of Exxon Research was to determine the oil content of samples collected from a spill using the carbon tetrachloride-infrared techniques developed for measuring parts per billion of oil in seawater.

EXPERIMENTAL

Sampling

A major goal of the program was to make quantitative measurements of the total oil, and the distribution of its fractions, in the water column. Requirements included background water samples, samples of the oil spilled, and the oil and water under the slick.

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*This work was done under contract with the American Petroleum Institute in support of a study to evaluate chemical dispersants in oil spill control.

Because the concentration of individual oil fractions in the water were likely to be very low, extreme caution was exercised to minimize contamination. Therefore, the 400 one-half gallon sample bottles for the determination of oil in water were fitted with teflon-lined caps and rinsed three times with carbon tetrachloride (CCl_4) before being sent to the research vessel. The cases of Burdick and Jackson, distilled in glass CCl_4 were all tested for purity by infrared (IR) before going to the vessel. Convenient apparatus for dispensing 25 ml of CCl_4 were also provided the sampling team.

On the ship, the surface water was sampled by bucket and the subsurface water with submersible pumps discharging through polypropylene tubing into the precleaned sample bottles which were aboard ship. The intake tubing was deployed before entering the oily area and retrieved outside the oil. The sample pumps operated continuously, so that the system was constantly flushed to help ensure the integrity of the sample.

Twenty-five ml of the special CCl_4 was added to each bottle as soon as possible after sampling and all of the samples were sent to Exxon Research at Linden when the research vessel docked. Personnel of Exxon Research were not involved in the sampling operations.

Method of Analysis

The basic analytical technique applied to this study is described in detail*. Figure A-1 is a schematic description of the method. The 1.5 liters of water were extracted with one 50-ml portion of CCl_4. The extract was placed in a 5 cm cell and scanned by a FT-IR instrument. The absorbance of the peak at 2930 cm^{-1} was measured and converted to micrograms of oil by means of a calibration factor based on over 30 different crude oils. This IR value measures other CCl_4 soluble lipids such as organic acids, esters, and alcohols in addition to petroleum.

In order to measure total nonvolatile (C_{14+}) hydrocarbons, the CCl_4 extract was evaporated to 2 ml and then separated in a silica gel column into a total hydrocarbon fraction as shown in Figure A-1. An infrared measurement of the final silica gel fraction provided a measure of the hydrocarbons.

RESULTS

Exxon Research agreed to provide 400 bottles and analyze 133 samples for extractable organics and 10 for nonvolatile hydrocarbons. Jay Johnson of JBF requested that 185 samples be analyzed for extractable organics. The results are presented in Tables A-2 through A-5. The background oil content of the testing area taken before the oil spills are not available, for these samples never reached the Linden laboratory. Backgrounds taken after the first and third oil spills are presented in Tables A-3 and A-5, respectively.

*R.A. Brown, J.J. Elliott, J.M. Kelliher, and T.D. Searl, "Sampling and Analysis of Nonvolatile Hydrocarbons in ocean Water," Adv. in Chem., No. 147, 172-187 (1975).

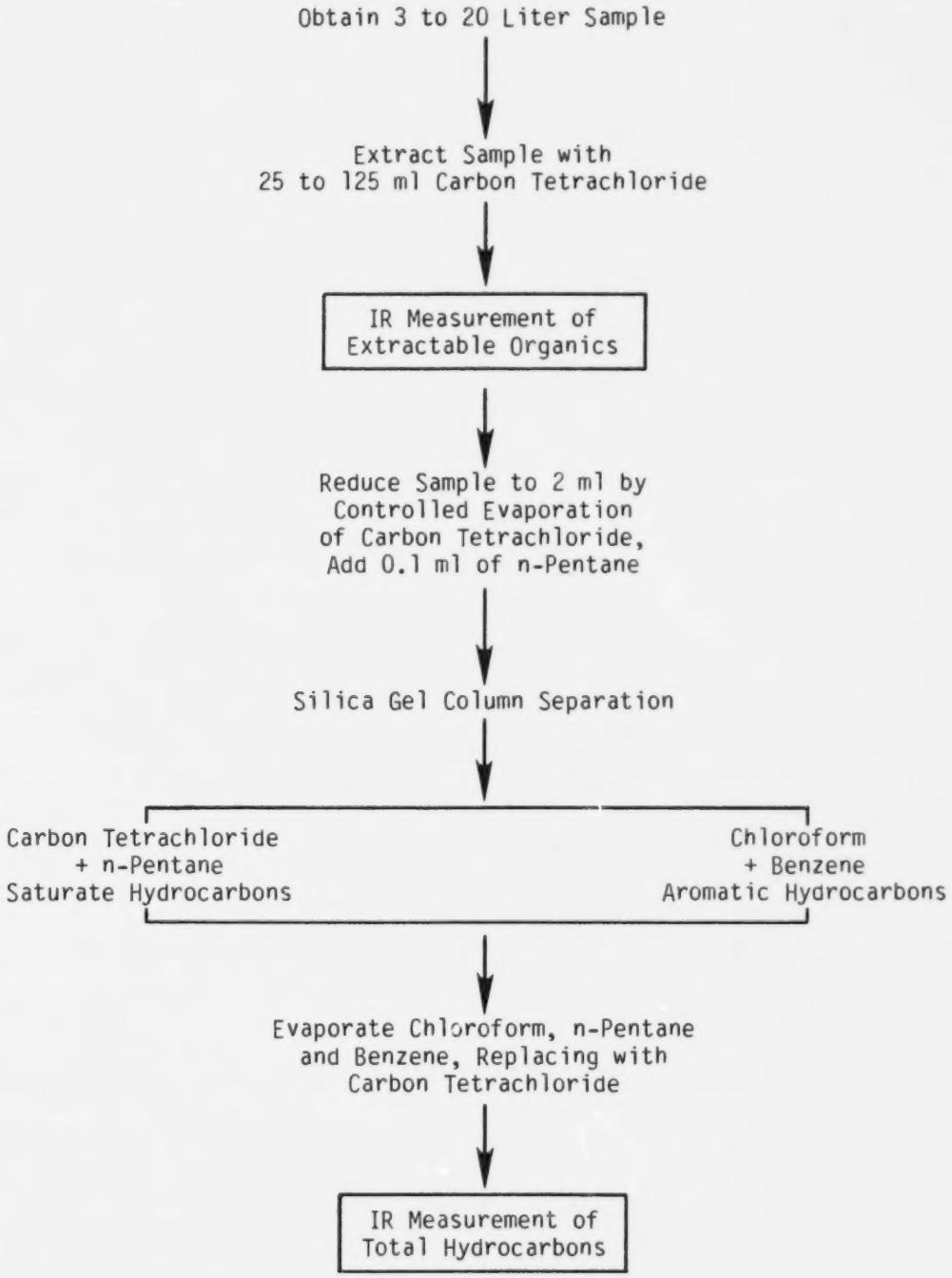

Figure A-1. Analytical method for nonvolatile hydrocarbons in ocean water.

In 1972, as part of Exxon's program on the measurement of hydrocarbons in the oceans of the world, tankers passing through this same area took surface and 10 m samples of seawater. The extractable organic values obtained for five samples are presented in Table A-6 and summarized in Table A-1 with the values obtained on the current tests.

The background values for surface and subsurface extractable organics obtained before the second spill are considerably higher than the values obtained before the fourth spill. Possibly some oil from Test I was still present in the water column. The agreement between the background data for the fourth spill and the tanker data obtained 6 years before are good: They are statistically similar.

The data for nonvolatile hydrocarbons obtained at three stations are given in Tables A-4 and A-5. A mean value of 0.68 is given by the ratio nonvolatile hydrocarbons/extractable organics. This is in the range normally observed.

TABLE A-1. COMPARISON OF BACKGROUND LEVELS OF EXTRACTABLE ORGANICS AT SPILL SITE

Description	Surface		Subsurface		
	EO	Std. Dev.	EO	Std. Dev.	Depth, M
	ug/l				
1972, Tanker	47	16	42	7	10
1978, Before 2nd Spill	517, 151	--	71	12	1,3,6,9
1978, Before 4th Spill	62	--	36	--	6,9

TABLE A-2. EXTRACTABLE ORGANICS IN WATER BY IR FIRST ATLANTIC OIL SPILL OF 11/2/78 WITH MURBAN CRUDE

Dispersant Added	Nominal Time after Spill, min.	Station	Actual Time	Extractable Organics in Water, µg/l				
				Surface	1m	3m	6m	9m
No	T + 15	1	12:13		951	29		
No	"	8	12:26	26,900		158	51	54
Yes	T + 120	1	14:23	105	24	49		
"	"	2	14:25			29		
"	"	3	14:28	92	119	107	137	119
"	"	5	14:33	51	45	48		
"	"	7	14:38	63	92	48		
"	"	9	14:44	479,000	113	72		
Yes	T + 180	1	15:01	1,950	41	46		
"	"	3	15:07	230	104	87	42	39
"	"	4	15:10	80	65	85		
Yes	T + 240	3	16:37	199	142			
"	"	4	16:42	270	125			
"	"	5	16:46	927	180			

TABLE A-3. EXTRACTABLE ORGANICS IN WATER BY IR SECOND ATLANTIC OIL SPILL OF 11/3/78 WITH LAROSA CRUDE

Dispersant Applied	Nominal Time after Spill, min.	Actual Time	Station	Extractable Organics in Water, µg/l				
				Surface	1m	3m	6m	9m
	Background			517	77	76	67	69
				151	58	93	56	73
No	0	10:32	3		220	507	116	34
No	T + 30	10:54	3		116	147	194	116
Yes	T + 120	12:19	1	144	219	65		
"	"	12:28	3	223	86	89	103	67
"	"	12:35	5	146	13	108		
Yes	T + 180	13:20	3	1,245	95	1,049	649	294
"	"	13:24	4	135				
"	"	13:33	6	96	93	102		
"	"	13:39	7	52	39	45		
Yes	T + 225	14:00	3	111	81	79		42
Yes	T + 300	15:33	9	67	59		49	

TABLE A-4. EXTRACTABLE ORGANICS IN WATER BY IR THIRD ATLANTIC OIL SPILL OF 11/9/78 WITH LAROSA CRUDE

Dispersant Applied	Nominal Time after Spill, min.	Actual Time	Station	Extractable Organics in Water, µg/l				
				Surface	1m	3m	6m	9m
Yes	T + 30	10:43	1	252	26	90		
"	"	10:51	3	10,800	1,950	2,750	498	99
"	"	10:58	4	4,060	957	668		
"	"	11:20	7	4,690	1,650	2,960		
"	"	11:23	8	7,050	2,240(a)	433	490	245
"	"	11:29	9	521	691	69		
"	"	11:34	10	1,760	64	45		
Yes	T + 90	11:43	1	100	180	62		
"	"	11:46	2	lost		161		
"	"	11:48	3	1,050	320	297	109	79
"	"	11:51	4		297	185		
"	"	11:54	5	106	64	50		
"	"	12:03	6	92				
"	"	12:07	7	1,630	642	1,130		
"	"	12:11	8	1,410	1,250(b)	288	305	
"	"	12:18	9			148		
Yes	T + 180	13:10	3	125	52	36	53	45
"	"	13:15	8	385	158	101	146	

(a) Nonvolatile hydrocarbon = 1,430 µg/l.

(b) Nonvolatile hydrocarbon = 718 µg/l.

TABLE A-5. EXTRACTABLE ORGANICS IN WATER BY IR FOURTH ATLANTIC OIL SPILL OF 11/9/79 WITH MURBAN CRUDE

Dispersant Applied	Nominal Time after Spill, min.	Actual Time	Station	Extractable Organics in Water, µg/l				
				Surface	1m	3m	6m	9m
Background	--	--	--	62	121		28	43
Yes	T + 30	14:32	2	20,500	6,100			
"	"	14:34	3	1,360,000	17,800		45	
"	"	14:40	4		3,170			
"	"	14:59	7	123		84		
"	"	15:02	8	11,000	3,800	2,540(a)	972	948
"	"	15:07	9		3,070			
Yes	T + 75	15:28	2	3,400	1,550			
"	"	15:32	3	7,290	3,810	3,720	302	352
"	"	15:54	6		81			
"	"	16:01	7	1,820	98	91		
"	"	16:06	8	960	294	310	329	182
"	"	16:11	9	409	201			
"	"	16:15	10	140	66	75		
Yes	T + 150	17:05	3	110	129	36	39	73
	"	17:15	8	339	138	147	119	128

(a) Nonvolatile hydrocarbons = 1,968 µg/l.

TABLE A-6. EXTRACTABLE ORGANICS IN COASTAL WATER BY TANKER

Date	Ship	Lat.	Long.	Extractable Organics µg/l Surface	10 M
11/2/79	Present Study	40° 10'	73° 35'	--	--
3/19/72	Esso Lexington	40° 07'	73° 44'	63	42
3/28/72	" "	39° 35'	73° 36'	42	--
4/12/72	Esso Puerto Rico	39° 54'	73° 44'	24	46
4/14/72	" " "	39° 38'	73° 45'	60	32
4/20/72	Esso Lexington	40° 06'	73° 39'	45	47
			Average	47	42

EXXON RESEARCH AND ENGINEERING COMPANY

P.O. BOX 121, LINDEN, N. J. 07036

ANALYTICAL AND INFORMATION DIVISION
J. K. PATTERSON
Director

May 23, 1979

Analytical Support to the
API Investigation of the
Effectiveness of Surface-
Active Agent in Combatting
Open Ocean Spills

Ref. No. 79AN 541

Dr. J. R. Gould
American Petroleum Institute
2101 L Street, NW
Washington, D. C. 20037

Dear Dr. Gould:

Our report on the above subject dated 4/2/79 presented analytical data on the extractable organics content of over 180 sea water samples, thus fulfilling the provisions of Exxon Research and Engineering Company's contract with the American Petroleum Institute. The Oil Spill Task Force, after receiving the report, requested that we analyze an additional 50 samples. The results of these analyses are presented in the attached table.

Very truly yours,

T. D. Searl

T. D. Searl

TDS:pjs

Attachment

cc: J. Johnson - JBF Corp.
G. P. Canevari

ADDITIONAL ANALYSES OF ATLANTIC OCEAN
PLANNED OIL SPILL SAMPLES - NOVEMBER, 1978

Test	Crude	Sample	Station	Approx. Time	Extractable Organics in Water, ppb				
					0 m	1 m	3 m	6 m	9 m
1	Murban	21	7	T + 15 min.	665				
	"	22	7	T + 15 min.			119		
	"	32	9	T + 15 min.	527				
	"	33	9	T + 15 min.			50		
	"	194	2	T + 3 hrs.	557				
	"	195	2	T + 3 hrs.		122			
	"	196	2	T + 3 hrs.			107		
	"	235	5	T + 3 hrs.	131				
	"	236	5	T + 3 hrs.		79			
2	LaRosa	239	6	T + 30 min.		102			
	"	357	6	T + 30 min.			126		
	"	414	6	T + 30 min.				68	
	"	413	6	T + 30 min.					63
	"	205	7	T + 30 min.		93			
	"	347	2	T + 2 hrs.	198				
	"	431	2	T + 2 hrs.		117			
	"	432	2	T + 2 hrs.			161		
	"	502	1	T + 3 hrs.	2,760				
	"	501	1	T + 3 hrs.		227			
	"	500	1	T + 3 hrs.			255		
	"	503	2	T + 3 hrs.	300				
	"	504	2	T + 3 hrs.		180			
	"	505	2	T + 3 hrs.			163		
	"	560	2	T + 3-3/4 hrs.	118				
	"	561	2	T + 3-3/4 hrs.		132			
	"	566	4	T + 3-3/4 hrs.	132				
	"	568	4	T + 3-3/4 hrs.		125			
3	LaRosa[(a)]	911	2	T + 30 min.	19,100				
	"	910	2	T + 30 min.		87			
	"	909	2	T + 30 min.			105		
	"	920	5	T + 30 min.	178				
	"	921	5	T + 30 min.		165			
	"	923	6	T + 30 min.	440				
	"	924	6	T + 30 min.		91			
	"	925	6	T + 30 min.			92		
	"	765	2	T + 1-1/2 hrs.		147			
	"	339	10	T + 1-1/2 hrs.		279			
4	Murban[(a)]	973	1	T + 30 min.	307				
	"	974	1	T + 30 min.		88			
	"	975	1	T + 30 min.			111		
	"	708	2	T + 30 min.			1,200		
	"	705	3	T + 30 min.			10,200		
	"	996	4	T + 30 min.	23,200				
	"	732	4	T + 30 min.			1,070		
	"	720	5	T + 30 min.		168			
	"	727	9	T + 30 min.	6,400				
	"	733	9	T + 30 min.			2,690		
	"	977	10	T + 30 min.	218				
	"	736	10	T + 30 min.		202			
	"	735	10	T + 30 min.			143		

[(a)] Dispersant added immediately after spill.

APPENDIX B

DATA FROM CHEVRON OIL FIELD RESEARCH CO.

Chevron Oil Field Research Company
A Standard Oil Company of California Subsidiary
P.O. Box 446, La Habra, CA 90631, U.S.A.

April 24, 1980

Mr. Jaret C. Johnson
JBF Scientific Corp.
2 Jewel Drive
Wilmington, MA 01887

Dear Jay:

Enclosed are the low-molecular-weight hydrocarbon analyses for the 1978 East Coast tests. Because of errors in electronic integration of the gas chromatograms, we measured peak heights and recalculated all the aromatic hydrocarbons. The tables include only those samples that had measurable concentrations over background values. All samples contained some GC peaks, but when measuring at a few parts per trillion sensitivity, it is easy to obtain contamination - from the air during sampling, from the containers, or during laboratory analysis.

These data can be included as an appendix to the report you prepare for API. You can also attach a copy of our paper and refer to it for an explanation of how the data were obtained. Refer also to the paper for use of the analysis in interpreting weathering of the Murban and La Rosa crude oils that occurred following discharge of these oils.

Sincerely,

Clayton

Clayton D. McAuliffe

Attach: Analyses

cc: J. R. Gould, API w/attach
G. P. Canevari, Exxon Research
J. P. Marum, AMOCO

TABLE B-1. API 1978 EAST COAST GAS CHROMATOGRAPH ANALYSIS, MURBAN, TEST 1. OIL SPILLED 1153-1200, DISPERSED 1350-1415

	Non-Dispersed							Dispersed		
Sample station	1	1	1	6	6	7	7	6	6	9
Sample number	126	129F	127	75	76	80	81	144	145F	162F
Depth, m	1	1	3	3	6 BKG	0	3	3	3	0
Time	1213	1213	1214	1219	1220	1221	1222	1436	1436	1444
Hydrocarbons, µg/L (ppb)										
Methane	.088	.061	.074	.126	.058	.065	.066	.097	.080	.064
Ethane	-	-	-	.090	-	-	.020	-	-	-
Propane	.005	.004	.007	.165	.004	.014	.040	-	.002	.002
Isobutane	.004	.004	-	.012	-	-	.008	-	-	.003
n-Butane	.014	.007	.008	.141	.005	.003	.035	.003	.005	-
Isopentane	.016	.006	-	.083	-	-	.017	-	.006	-
n-Pentane	.027	.010	-	.076	.002	.004	.023	.009	.004	-
Cyclopentane	.023	.005	-	.055	-	-	.012	-	.006	-
3-Methylpentane	.007	-	-	.022	-	-	-	-	.006	-
n-Hexane	.019	.004	-	.027	-	-	.012	-	.012	-
Methylcyclopentane	.029	.009	-	.016	-	-	.010	-	.027	.008
Benzene	.325	.203	-	.97	-	.073	.137	-	.155	.023
Cyclohexane	.039	.024	.036	-	-	-	.023	-	.040	-
n-Heptane	.013	-	-	-	-	-	-	-	-	-
Methylcyclohexane	.037	.020	-	.007	-	.018	-	-	.022	.020
Toluene	.975	.980	.250	.67	.113	.58	-	.187	.25	.169
Ethylbenzene	.26	.22	.155	.166	.137	.20	.121	.154	.118	1.10
m, p-Xylene	.84	.78	.57	.60	.51	.67	.47	.69	.48	5.29
O-Xylene	.54	.53	.37	.37	.32	.43	.26	.89	.37	6.48
926 Trimethylbenzene	-	-	-	-	-	-	-	.021	.011	.70
1027 Trimethylbenzene	.21	.26	.153	-	.123	.171	.109	.22	.177	17.6
1077 Trimethylbenzene	.050	.077	-	-	.088	.052	.020	.22	.091	9.6
1,2,4-Trimethylbenzene	.165	.25	.137	-	.110	.155	.111	.52	.159	-
1197 Trimethylbenzene	.105	.113	.070	-	.070	.040	.035	.079	.040	12.9
TOTAL	3.80	3.56	1.83	3.60	1.54	2.84	1.71	3.09	2.06	54.0

TABLE B-2. API 1978 EAST COAST GAS CHROMATOGRAPH CHEMICAL ANALYSIS, TEST 3 LA ROSE
OIL SPILLED 1019, OIL DISPERSED 1028

Sample station	3	3	3	3	4	4	4	7	7	7	7	7	8	8	2	3	7	7	7	7	7	7	3
Sample number	936	938	940	943F	860	866	864	878	879F	880	882	883F	886	887F	788	786	800	801F	822	823F	828	829F	699
Depth, m	0	1 m	3 m	6 m	0	1 m	3 m	0	0	1 m	3 m	3 m	1 m	1 m	3 m	1 m	0	0	1 m	1 m	3 m	3 m	3 m
Time	1051	1051	1052	1052	1058	1059	1059	1120	1120	1120	1121	1121	1124	1124	1147	1149	1207	1207	1207	1207	1208	1208	1311
Hydrocarbons, µg/L (ppb)																							
Methane	.082	.119	.057	.153	.060	.059	.121	.045	.073	.057	.071	.053	.064	.071	.069	.124	.095	.077	.053	.063	.060	.076	.053
Ethane	-	-	-	-	-	-	-	.079	.070	.053	.065	.083	-	.042	-	-	-	.064	.046	.027	.052	.045	-
Propane	.152	.026	.007	.042	-	.004	.027	.38	.38	.30	.38	.36	.024	.23	.002	.015	.36	.30	.164	.109	.242	.187	-
Isobutane	.032	.017	.002	.009	-	-	.018	.75	.25	.197	.28	.25	.018	.154	-	-	.24	.20	.090	.062	.154	.115	-
n-Butane	.189	.061	.009	.055	-	-	.067	.69	.57	.52	.68	.59	.048	.37	-	.051	.64	.48	.27	.160	.409	.261	-
Isopentane	.151	.069	.009	.038	-	-	.066	.66	.47	.51	.64	.54	.075	.27	-	.047	.59	.38	.24	.123	.360	.207	-
n-Pentane	.140	.042	.010	.038	-	.003	.053	.65	.35	.48	.59	.45	.083	.17	.003	.040	.60	.33	.26	.110	.365	.169	-
Cyclopentane	.193	.047	.009	.034	-	-	.072	.70	.43	.53	.60	.52	.101	.23	-	.020	.60	.35	.31	.128	.365	.170	-
3-Methylpentane	.073	.016	.004	.007	.015	-	.031	.26	.13	.191	.22	.18	.040	.071	-	.011	.23	.12	.106	.037	.135	.054	-
n-Hexane	.121	.017	.010	.006	-	-	.051	.41	.13	.28	.33	.23	.070	.065	-	.011	.42	.17	.192	.048	.250	.073	-
Methylecyclopentane	.193	.017	-	.004	-	-	.051	.75	.46	.57	.60	.57	.111	.24	-	-	.56	.34	.39	.145	.335	.180	-
Benzene	.47	-	-	-	-	.25	-	1.47	.60	1.23	1.16	.50	.26	.45	-	-	.90	.37	.70	.250	.185	.203	.090
Cyclohexane	.28	-	-	.066	-	-	-	1.23	.63	.07	.07	.76	.18	.29	-	-	.80	.37	.57	.175	.46	.187	-
n-Heptane	1.02	-	-	.003	-	-	.062	.23	.09	.149	.142	.091	.013	.21	-	-	.26	.074	.128	.092	.23	.030	-
Methylcyclohexane	.51	.037	-	-	-	-	.122	1.03	.49	.89	.89	.51	.26	.22	-	-	.07	.36	.59	.144	.61	.168	-
Toluene	1.14	.250	.171	.146	.189	.096	.24	2.86	1.80	2.43	2.27	1.50	.24	1.09	.171	.070	2.15	1.11	1.46	.54	1.63	.57	.24
Ethylbenzene	.41	.122	.078	.013	.070	.035	.157	.89	.66	.73	.66	.59	.156	.32	.070	.051	.106	.41	.39	.126	.30	.195	.053
m, p-Xylene	1.09	.46	.33	.20	.28	.24	.49	2.17	1.75	1.93	1.63	1.40	.48	.84	.30	.23	.24	1.04	.97	.35	.97	.51	.26
o-Xylene	.87	.36	.26	.145	.26	.26	.45	1.58	1.30	1.32	1.20	1.05	.35	.62	.20	.26	.95	.77	.72	.27	.72	.40	.130
926 Trimethyl-benzene	.079	-	-	.014	-	-	.047	.22	.15	.173	.158	.14	.10	.063	.003	.08	.21	.007	.064	.025	.064	.045	-
1027 Trimethyl-benzene	.68	.28	.28	.035	.19	.16	.34	1.24	.94	.99	.87	.66	.28	.40	.20	.15	.66	.61	.41	.138	.35	.43	.063
1077 Trimethyl-benzene	.170	.051	.038	.023	.33	.030	.077	.33	.35	.28	.26	.20	.077	.164	.22	.100	.21	.182	.130	.057	.104	.096	-
1,2,4-Trimethyl-benzene	.78	.36	.31	.114	.31	.22	.56	.112	1.15	1.40	.02	.64	.31	.48	.22	.137	.71	.67	.45	.148	.51	.34	.14
1197 Trimethyl-benzene	.53	.27	.089	.073	.21	.143	.32	1.50	.90	1.17	.89	.47	.32	.37	.036	.105	.61	.51	.32	.063	.40	.27	-
Total	8.46	2.62	1.67	1.22	1.91	1.51	3.42	20.3	14.2	17.3	16.5	12.8	3.56	7.43	1.36	1.41	13.2	9.37	9.02	3.39	9.35	4.95	1.03

TABLE B-3. API 1978 EAST COAST GAS CHROMATOGRAPH CHEMICAL ANALYSIS, MURBAN, TEST 4, RUN 1.
OIL SPILLED 1404, DISPERSED 1411-1416.

Sample station	2	2	2	2	2	2	3	3	3	3	4	4	4	4	4	4	4	8	8
Sample number	838	839F	835	836F	834	837F	1153	1166	1165F	1161	1162F	978	983F	979	982F	980	981F	1145	1149F
Depth, m	0	0	1	1	3	3	0	1	1	3	3	0	0	1	1	3	3	0	0
Time	1432	1432	1432	1432	1433	1433	1434	1435	1435	1435	1435	1440	1440	1440	1440	1441	1441	1502	1502
Hydrocarbons, µg/L (ppb)																			
Methane	.124	.097	.069	.058	.074	.100	.21	.079	.24	.068	.089	.082	.101	.071	.061	.062	.060	.059	.077
Ethane	-	-	-	-	-	-	-	-	-	-	.004	-	-	-	-	-	-	-	-
Propane	.018	.014	.009	.002	.008	.020	.018	.006	.039	-	.016	.014	.020	.006	.007	.011	.006	-	.009
Isobutane	.004	.009	-	.003	-	.006	-	-	-	-	.008	.004	.016	.003	.008	.002	-	-	.006
n-Butane	.040	.024	.014	.003	.007	.023	.003	.010	-	-	.006	.015	.085	.004	.009	.012	.017	-	.004
Isopentane	.043	.036	.002	-	.006	.003	.007	-	-	-	.003	.015	.035	.006	.004	.005	-	-	.001
n-Pentane	.138	.076	.006	.004	.004	.020	.021	.003	.125	.002	.007	.032	.050	.015	.015	.011	-	.007	.007
Cyclopentane	.60	.42	-	.004	-	-	.173	.012	.150	.011	.004	.058	.054	.023	.005	.015	.004	.034	.026
3-Methylpentane	.46	.28	-	-	-	-	.139	.007	.117	.004	.010	.032	.023	.010	.004	.008	-	.019	.023
n-Hexane	2.1	.89	-	.007	.005	-	.97	.046	.121	.028	.024	.142	.061	.046	.004	.035	.029	.102	.072
Methylcyclopentane	2.2	1.42	-	-	.006	.006	1.20	.054	.150	.025	.036	.107	.085	.041	.010	.025	.131	.102	.092
Benzene	-	-	.041	.038	.083	.061	.66	.165	.183	.23	.117	.20	.21	.165	.162	.23	.084	.26	.26
Cyclohexane	8.7	5.12	.006	-	.045	.021	.51	.160	.063	.071	.139	.27	.100	.086	.037	.075	.027	.27	.21
n-Heptane	17.3	4.65	-	-	-	.025	50.	.47	-	-	.128	.84	-	.23	-	-	-	.67	.34
Methylcyclohexane	18.9	9.35	-	.021	-	.045	47.	.67	.161	.195	.315	1.00	.26	.28	.057	1.15	.034	.91	.59
Toluene	170.	99.2	.122	.107	2.1	.70	950.	4.80	1.37	2.15	3.50	6.70	2.2	2.40	.81	1.40	.43	5.70	3.75
Ethylbenzene	56.	43.	.079	-	1.29	.33	420.	2.70	.97	.96	2.20	4.10	1.44	1.33	.51	.60	.27	1.90	2.25
m, p-Xylene	370.	118.	.22	.094	10.3	1.15	1510.	14.9	3.15	5.50	8.85	15.8	2.90	5.90	1.66	2.00	.84	11.7	7.70
o-Xylene	137.	84.	.18	.070	3.4	.86	700.	8.5	2.40	1.86	5.65	7.60	3.10	2.70	1.31	1.19	.62	4.75	5.45
926 Trimethylbenzene	14.2	5.6	-	-	1.61	.063	.50	3.2	.14	.10	.50	2.30	.24	.14	.10	.10	.033	.44	.42
1027 Trimethylbenzene	135.	65.	.36	-	11.9	.90	4.6	15.6	1.76	1.60	8.95	17.3	2.70	6.80	.99	1.17	.39	7.95	6.50
1077 Trimethylbenzene	59.	30.	-	-	-	.36	1.91	6.9	.84	-	3.90	7.4	1.35	1.10	.51	.44	.166	2.90	2.75
1,2,4-Trimethylbenzene	102.	57.	1.03	-	32.	.86	3.4	2.2	1.65	3.30	7.50	2.3	2.30	7.00	.96	.90	.38	4.50	6.20
1197 Trimethylbenzene	53.	26.	.48	-	17.9	.55	1.49	11.6	.85	.42	4.60	13.1	1.30	1.22	.56	.64	.22	3.90	3.20
TOTAL	1147.*	550.	2.61	.41	80.7*	6.2	3693.*	72.1*	14.5	16.6	46.5	79.4*	18.6	29.6*	7.8	10.1	3.7	46.2	39.9

* FREE OIL IN SAMPLE.

TABLE B-3 (CONT.) API 1978 EAST COAST GAS CHROMATOGRAPH CHEMICAL ANALYSIS, MURBAN, TEST 4, RUN 1.
OIL SPILLED 1404, DISPERSED 1411-1416

Sample station	8	8	8	8	8	8	8	8	9	9	9	9	9	9	10	10	10	10
Sample number	1150	1154F	1144	1155F	1115	1159F	1119	1160F	1113	1117F	1114	1118F	1111	1107F	1101	1102	1120F	1103
Depth, m	1	1	3	3	6	6	9	9	0	0	1	1	3	3	0	1	1	3
Time	1502	1502	1503	1503	1504	1504	1505	1505	1507	1507	1507	1507	1508	1508	1510	1511	1511	1512
Hydrocarbons, µg/L (ppb)																		
Methane	.066	.070	.061	.072	.055	.070	.057	.073	.071	.145	.073	.047	.060	.096	.064	.196	.064	.058
Ethane	-	.002	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Propane	-	.004	-	-	-	-	-	-	.009	.029	.010	.010	.003	.014	-	.017	.003	-
Isobutane	-	.003	-	-	-	-	-	-	-	-	.002	.007	-	-	-	.003	.002	-
n-Butane	-	.002	-	-	-	-	-	-	.012	.23	.018	.009	.003	.049	-	.012	.003	-
Isopentane	-	.002	-	-	-	-	-	-	.012	.125	.033	.012	.002	.019	-	-	-	-
n-Pentane	.002	.005	-	-	.019	-	-	-	.021	.075	.073	.022	.006	.033	-	.009	.006	-
Cyclopentane	.007	.012	.009	-	-	-	-	-	.042	.125	.172	.060	.009	.042	-	-	.022	-
3-Methylpentane	-	.006	.006	-	-	-	-	-	.019	.060	.096	.031	-	.031	-	-	-	-
n-Hexane	.035	.022	.043	-	.003	-	-	-	.084	.119	.37	.064	.020	.031	-	-	.003	-
Methylcyclopentane	.029	.027	.038	-	-	-	-	-	.055	.125	.33	.083	.016	.026	-	-	.003	-
Benzene	.138	.095	.43	.041	-	-	-	-	.24	.30	.55	.56	.21	.20	.040	-	.069	-
Cyclohexane	.099	.066	.037	.011	-	.041	-	-	.128	.089	.80	.155	-	-	-	-	-	-
n-Heptane	.160	.067	.25	.008	.029	.018	-	-	.138	-	1.04	.082	-	-	-	-	-	-
Methylcyclohexane	.30	.135	.44	.040	.092	.020	.012	-	.22	.038	1.29	.188	.072	.031	.007	.009	.013	.005
Toluene	2.05	1.40	3.0	.395	.58	.48	.38	.26	1.61	.95	6.90	3.95	.42	.56	.100	.165	.190	.133
Ethylbenzene	.96	.80	1.41	.285	.295	.23	.24	.075	.45	.29	2.20	1.11	.26	.24	.105	.157	.166	.157
m, p-Xylene	4.50	2.55	6.65	1.05	1.02	.95	.85	.50	1.43	.89	11.4	3.70	.87	.70	.29	.54	.66	.54
o-Xylene	2.05	1.85	2.85	.75	.61	.57	.52	.24	.84	.64	5.65	2.55	.49	.73	.23	.32	.41	.29
926 Trimethylbenzene	.173	.12	.30	.050	.031	.035	.032	.023	.063	.038	.38	.12	.032	.043	-	.032	.021	-
1027 Trimethylbenzene	2.20	1.55	3.40	.74	.37	.50	.41	.027	.68	.42	10.3	1.45	.34	.29	.062	.220	.32	.125
1077 Trimethylbenzene	.82	.65	1.39	.30	.20	.16	.154	.035	.28	.147	1.75	.70	.13	.14	-	.077	.116	-
1,2,4-Trimethylbenzene	1.75	1.40	2.65	.75	.45	.31	.45	.065	.64	.31	5.35	1.35	.42	.29	.056	.220	.35	.140
1197 Trimethylbenzene	1.18	.66	2.00	.38	.25	.13	.18	.040	.36	.156	2.05	.65	.43	.13	-	.143	.19	.036
TOTAL	16.5*	11.4	24.8	4.87	4.00	3.51	3.29	1.34	7.40	5.30	50.8	16.9	3.79	3.70	.95	2.12	2.61	1.48

* FREE OIL IN SAMPLE

TABLE B-4. API 1978 EAST COAST GAS CHROMATOGRAPH CHEMICAL ANALYSIS, MURBAN, TEST 4, RUN 2.
OIL SPILLED 1404, DISPERSED 1411-1416

Sample station	2	2	2	2	3	3	3	3	3	3	3	3	3	6	8	8	8
Sample number	1175	1179	1180F	1174	1063	1068	1069	1067	1070	1073	1074	1077	1078	655	666	664	665F
Depth, m	0	1	1	3	0	1	1	3	3	6	6	9	9	1	0	1	1
Time	1528	1529	1529	1530	1532	1533	1533	1534	1534	1535	1535	1535	1535	1555	1606	1606	1606
Hydrocarbons, µg/L (ppb)																	
Methane	.020	.150	.104	.057	.121	.065	.071	.068	.069	.066	.066	.084	.074	.072	.128	.078	.127
Ethane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Propane	-	.040	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Isobutane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
n-Butane	-	.007	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Isopentane	-	.008	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.008
Cyclopentane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.006
3-Methylpentane	-	.008	.008	-	-	-	-	-	-	-	-	-	-	-	-	-	.004
n-Hexane	-	.018	.006	-	-	-	-	-	-	-	-	-	-	-	-	-	.008
Methylcyclopentane	-	.014	.018	-	-	-	-	-	-	-	-	-	-	-	-	-	.008
Benzene	-	.069	.020	-	-	-	-	-	-	-	-	-	-	-	-	-	.006
Cyclohexane	-	.027	.041	-	-	-	-	-	-	-	-	-	-	-	-	-	.024
n-Heptane	-	-	-	-	.022	.033	.035	-	.034	-	-	-	-	-	-	-	.040
Methylcyclohexane	-	.052	.014	-	.088	.085	.084	.061	.108	-	.033	-	-	-	-	-	-
Toluene	.110	.79	.55	.22	1.24	1.28	1.40	1.21	1.38	.52	.73	.35	.38	.180	.030	.020	.150
Ethylbenzene	.30	.74	.42	.33	1.05	1.24	1.49	1.22	1.34	.75	.75	.40	.37	.160	.020	.018	.090
m, p-Xylene	1.02	2.50	1.80	1.09	5.50	5.20	7.50	4.90	5.90	2.70	2.55	1.42	1.36	.58	.150	.12	.429
o-Xylene	.86	1.81	1.13	.76	2.45	3.00	3.45	2.95	3.20	1.81	1.81	.96	.86	.25	.18	.15	.300
926 Trimethylbenzene	-	.17	.075	-	.29	.27	.35	.24	.32	.20	.16	.080	.072	-	-	-	.029
1027 Trimethylbenzene	.75	1.92	1.06	.68	7.90	6.70	8.70	3.30	7.50	2.00	1.84	.94	.92	.22	.172	.140	.051
1077 Trimethylbenzene	.36	0.88	.51	.27	1.49	1.50	1.62	1.35	1.54	1.74	.79	.39	.34	.051	.064	.051	.078
1,2,4-Trimethylbenzene	.78	1.71	1.13	.60	2.60	4.20	5.00	2.75	4.60	1.26	1.60	.83	.46	.21	.140	.070	.175
1197 Trimethylbenzene	.36	1.10	.68	.41	2.60	1.75	2.05	1.42	1.89	2.20	-	-	-	.071	.179	.036	.120
TOTAL	4.56	12.0	7.31	4.42	25.3	25.3	31.8	19.5	27.9	13.0	10.3	5.45	6.06	1.79	.86	.38	1.53

TABLE B-4 (CONT.). API 1978 EAST COAST GAS CHROMATOGRAPH CHEMICAL ANALYSIS, MURBAN, TEST 4, RUN 2. OIL SPILLED 1404, DISPERSED 1411-1416.

Sample station	8	8	8	8	8	9	9	9	10
Sample number	662	663F	1104	1109F	1105	1116	639	642	636F
Depth, m	3	3	6	6	9	0	1	3	0
Time	1607	1607	1608	1608	1608	1611	1611	1612	1615
Hydrocarbons, µg/L (ppb)									
Methane	.134	.087	.076	.090	.065	.068	.064	.158	.061
Ethane	-	-	-	-	-	-	-	-	-
Propane	-	-	-	-	-	-	-	-	-
Isobutane	-	-	-	-	-	-	-	-	-
n-Butane	-	-	-	-	-	-	-	-	-
Isopentane	-	.008	-	-	-	-	-	-	-
n-Pentane	-	.006	-	-	-	.002	-	-	-
Cyclopentane	-	.004	-	-	-	-	-	-	-
3-Methylpentane	-	.008	-	-	-	-	-	-	-
n-Hexane	-	.008	-	-	-	-	-	-	-
Methylcyclopentane	-	.006	-	-	-	-	-	.005	-
Benzene	-	.024	-	-	-	.064	.070	.165	.045
Cyclohexane	-	.040	-	.045	-	-	-	-	-
n-Heptane	-	-	-	-	-	-	-	-	-
Methylcyclohexane	-	.039	-	.038	-	-	.002	-	-
Toluene	.118	.166	.79	.20	.20	.096	.32	.103	.093
Ethylbenzene	.105	.066	.140	.119	.117	.074	.087	.070	.041
m, p-Xylene	.45	.33	.55	.42	.43	.31	.33	.174	.190
o-Xylene	.25	.26	.35	.35	.38	.29	.21	.23	.20
926 Trimethylbenzene	-	.029	-	.011	.011	-	-	-	.017
1027 Trimethylbenzene	.23	.051	.31	.20	.14	.185	.14	.20	.018
1077 Trimethylbenzene	.064	.078	.11	.11	-	.038	.026	.039	.015
1,2,4-Trimethylbenzene	.20	.18	.28	.24	.15	.170	.14	.168	.016
1197 Trimethylbenzene	.089	.143	.14	.15	.089	.089	.071	.107	.032
TOTAL	1.65	1.79	4.17	1.97	1.58	1.39	1.46	1.42	.73

APPENDIX C

THE DISPERSION AND WEATHERING OF CHEMICALLY TREATED CRUDE OILS ON THE SEA SURFACE

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Four research crude oil spills discharged on the open ocean were chemically treated with a dispersant. The underlying water was then analyzed to determine (1) the dispersion of oil into the water column, and (2) the rate of loss (weathering) of low-molecular-weight hydrocarbons from the dispersed oil. These tests, funded by the American Petroleum Institute and the U. S. Environmental Protection Agency, were conducted in a manner similar to those for untreated spills conducted in 1975 (Ref. 1, 2). The current tests were designed to compare the dispersion and weathering of chemically treated and naturally dispersed oils.

The untreated oils (Ref. 1, 2) showed relatively low concentrations of nonvolatile hydrocarbons in the water column under the slicks, generally less than 1 mg/L. These samples containing naturally dispersed oil showed very rapid weathering of the C_1 to C_{10} hydrocarbons (<30 min). The C_1-C_{10} hydrocarbons detected were residual in the oil droplets, and truly dissolved hydrocarbons were apparently not present. Samples of oil collected over time from the surface slicks showed slower weathering (>7 hrs for trimethylbenzenes).

Chemical dispersion is thought to accelerate the natural weathering processes. This would result in higher concentrations of oil penetrating

to greater depths, and accelerated escape of volatile hydrocarbons to the atmosphere. The mechanism for this behavior was expected to be the mixing of dispersed droplets having high specific surface areas in near-surface water, causing rapid loss of volatile hydrocarbons. An untreated slick, although constantly exposed to the atmosphere, may be less susceptible to evaporation than dispersed oil because its lower surface-to-volume ratio tends to retard transport (by diffusion) of volatile hydrocarbons.

Oil emulsified in water is removed from most of the wind's influence, so that it does not travel as far as a surface slick. This minimizes the possibility of oil stranding or entering biologically sensitive areas. A review and discussion of the alteration of oil on a water surface is given in Reference 3.

The current study also involved extensive aerial remote sensing, and a limited biology program. This report, however, covers mainly the chemical results, plus limited observations made visually and from aerial photographs.

EXPERIMENTAL METHODS

General Operations

In November 1978, four spills were conducted approximately 40 km (25 mi) off New Jersey and 96 km (60 mi) south of Long Island, New York. Each spill was approximately 1.67 m3 (440 gal) of one of two crude oils (Murban from Abu Dhabi and La Rosa from Venezuela). These were the same crudes used for the 1975 untreated tests. Composition of the naphtha fraction is given in Reference 2.

Each spill was discharged from a 1.9 m3 (500 gal) tank mounted on the research vessel through two 7.6 cm (3 in) hoses. The ends of the hoses were on floats, causing the oil to discharge horizontally on the water surface. This minimized both evaporation losses due to discharge above the water, and vertical descent of the oil into the water. The less viscous Murban (0.83 specific gravity, 39° API) discharged in approximately 3 min; the La Rosa (0.91 specific gravity, 23.9° API), in 6 min.

The oils were treated by aerially spraying a self-mix dispersant from a pod and spray booms mounted above the skids of a helicopter. The helicopter flew approximately 10 m above the water surface. One slick of each oil was dispersed immediately, and one each after 2 hr.

The immediately dispersed slicks were sprayed with 150 L (40 gal) of chemical dispersant; the slicks sprayed after 2 hr with 360 L (95 gal). In all cases, there was over-spraying (outside the slick) and a percentage loss due to wind drift. The major experimental conditions are summarized in Table C-1.

Sample collection

The sampling program was designed to obtain water samples at approximately equally spaced stations on transects through the surface slicks and

TABLE C-1
GENERAL EXPERIMENTAL SUMMARY

Item	Murban 1	La Rosa 1	La Rosa 2	Murban 2
Date of spill	2 Nov. 1978	3 Nov. 1978	9 Nov. 1978	9 Nov. 1978
Time of spill	1153	1014	1019	1404
Time of dispersion	1350	1200	1028	1411
Spill location				
latitude	40°09'09"N	40°09'12"N	40°09'18"N	40°09'30"N
longitude	73°30'39"W	39°33'40"W	73°32'00"W	73°34'45"N
Conditions				
wave height, m	0.3 to 1.0	0.3 to 1.0	0.3 to 1.0	0.3 to 1.0
wind (m/s)	4.0 to 5.5	4.0 to 5.5	2.5 to 6.0	2.5 to 6.0
(knots)	8 to 11	8 to 11	5 to 12	5 to 12
air temp., °C	15-20	15-20	12-14	14-17
water temp., °C	14	14	13	13

emulsion plumes. Figure C-1 is a schematic diagram of a typical sample run. Samples of all four tests were taken at 1 and 3 m depths at all 10 stations, and at 6 and 9 m at Stations 3 and 8. Surface samples were taken, with a small bucket, at all stations during sampling runs through dispersed oil. A sampling run took about 45 min.

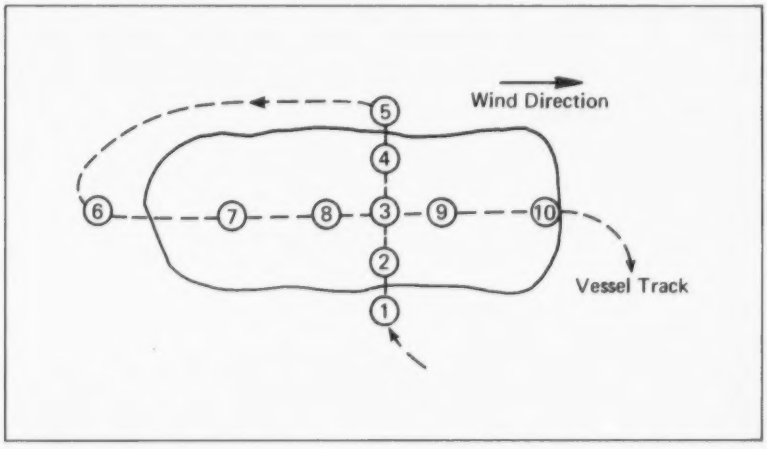

Fig. C-1 Schematic of immediately dispersed oil slick and location of sample stations for typical 10-station sample run.

For the immediately dispersed slicks, the first run was started a few minutes after dispersion, and the second after about 1.3 hr. For the two delayed dispersion tests, one sampling run was made before dispersion (untreated oil), and two after. The two sampling runs after dispersion were immediate and after about 1 hr.

For all of the spills a few samples were also taken 2, 3 and 4 hr after dispersion, at Stations 3 and 8.

The subsurface samples were collected with small submersible pumps discharging through polypropylene tubing, at approximately 4 L/min. The pumps were attached approximately 0.5 m below a floating 115 L (30 gal) steel drum towed 3 m lateral to the bow of the research vessel. In this position, the ship's bow wave did not cause water mixing at the sample inlets. These were 1, 3, 6 and 9 m below the water surface, along a line suspending a 23 kg weight from the bottom of the float. The sample gear was lowered and removed from the water outside the observed slicks to avoid surface oil contamination.

Two types of samples were collected at each station and depth: one 1.5 L sample in 1.9 L (0.5 gal) flint glass jug and duplicate completely filled 300 mL (10 oz) "soft drink" bottles with crown caps. The 1.9 L jugs had been cleaned by rinsing three times with distilled-in-glass carbon tetrachloride (CCl_4) that was checked for purity by infrared (IR) spectroscopy. Immediately after collection, 50 mL of this CCl_4 was added to each jug from an all-glass dispensing pipet. The jugs were sealed with teflon-lined metal screw caps, and hand-shaken for about 10 sec to initiate the solvent extraction of organic matter including the dispersed oil. The CCl_4 also prevented bacterial degradation of the hydrocarbons. In the laboratory, the samples were shaken 2 min to complete the extraction.

Prior to sample collection, about 30 mg of mercuric chloride ($HgCl_2$) was added to each 300 mL bottle to prevent biodegradation prior to analysis. Each bottle was then flushed with reactor-grade helium and sealed with a crown cap (polyvinyl chloride seal). At time of sample collection, each bottle was uncapped, filled to within 3 mm of the top, and resealed with a crown cap. The small air space minimized loss of volatile hydrocarbons to this gas space and possible contamination of sample by hydrocarbons (as well as CCl_4 vapors) that may have been in the atmosphere during sample collection.

Samples of each crude oil were taken from the spill tank in glass bottles with teflon-lined screw caps. In the laboratory these oil samples were equilibrated with sea water collected outside the spill area, to provide equilibrium dissolved hydrocarbon concentrations in sea water.

Aerial control and photography

A small twin-engine high-wing aircraft served as a control platform from which to direct the dispersant-spraying helicopter, to direct the research vessel to each sampling station, and to provide visual and photographic documentation of the oil slicks and their chemical dispersion. Periodic color photographic runs were made over each slick using a vertically mounted camera in the floor of the aircraft. Each exposure recorded the time and Loran C coordinates.

Chemical analysis

Total extractable organic matter was measured on the single 50 mL portion of CCl_4, with an IR instrument, as absorbancy at 2930 cm 1. This method measures other CCl_4 soluble compounds such as organic acids, esters,

and alcohols in addition to the crude oil. The CCl_4 extracts of a few samples were further analyzed for total nonvolatile (C_{14}+) hydrocarbons, by removing polar organic compounds with a silica gel column and reanalysis by IR. Details of these techniques are given in Reference 4.

Volatile hydrocarbons (C_1 to C_{10} fraction) in the water samples were analyzed by a gas equilibrium method (Ref. 5). Forty millilitres of Murban and La Rosa oil samples were equilibrated with 140 mL of sea water collected prior to the oil spills. The oil and water were hand shaken gently and periodically for 24 hr or more. Mercuric chloride added at the time of water collection prevented possible biodegradation of dissolved hydrocarbons during equilibration and prior to analysis. This water was filtered (from one 50 mL glass syringe into a second) to remove any separate-phase oil that may have been dispersed during oil-water mixing. Twenty-five millilitres of this water was gas equilibrated five times.

These successive analysis were used to measure the equilibrium concentrations of individual C_1 to C_{10} hydrocarbons for the two crude oils, and to calculate individual hydrocarbon distribution coefficients.

The water samples collected at the various stations and depths were then analyzed with a single equilibration using the measured distribution coefficients to calculate concentrations. This gives sufficient accuracy and saves time and cost of multiple equilibrations. For those samples that contained significant separate phase oil, the duplicate sample was filtered and analyzed. Separate-phase oil contributes hydrocarbons to the gas phase in concentrations higher than if the hydrocarbons were only in solution. Method details are given in References 1 and 5.

RESULTS AND DISCUSSION

Visual and photographic observations

Application of dispersant after two hours of weathering appeared to have little effect on Murban crude oil, based on visual and photographic observations. Dispersal of weathered La Rosa crude oil did appear effective. However, some oil reappeared within 10 to 15 min after dispersant application.

When dispersant was applied to fresh La Rosa, no sudden change was apparent. However, in time this oil became a thin sheen, as contrasted with the thick, black, asphaltic appearance of untreated La Rosa. Also, the track of the research vessel remained visible for a considerable period of time as contrasted with the quick closing behind the vessel with the untreated oil.

Murban crude oil changed dramatically when dispersant was immediately applied. A distinct whitish-brown subsurface plume appeared quickly. Over several hours, this plume dispersed in the water column, growing in area and diminishing in color and visibility. A thin-transparent surface oil sheen gradually appeared during this time period as some of the emulsion

droplets resurfaced and broke. These visual observations give qualitative indication of the dispersion of crude oils by chemical treatment, but chemical analysis is needed for quantitative interpretation.

Oil dispersion as determined by infrared analysis

The large number of chemical analyses prevents a complete tabulation of the results for total extractable organic matter (OM). Some of the analyses will be presented in graphical form to document chemical dispersion of these crude oils. As expected, the highest concentrations in the water column were attained after immediate dispersion as compared with dispersion after two hours. Interpretation will concentrate on immediate dispersion results.

The crossed transects of a sampling run permit a three-dimensional analysis of plumes of dispersed oil (i.e., in crossed vertical planes). However, the limited sampling at 6 and 9 m (only at Stations 3 and 8) may give a distorted (narrow) view of dispersion at these depths. Based upon natural dispersion of oil into the water column (Ref. 2) and the lack of chemically dispersed oil at 6 m (Ref. 6), significant dispersion of oil down to 6 and 9 m was not expected. These depths were added only to verify the prior results, but we were surprised to find measurable oil at 6 and 9 m. In subsequent studies conducted in September and October 1979, all stations were sampled through 9 m.

Fig. C-2 shows the extractable OM concentrations with depth along the two transects of the first sampling run following the immediate dispersion of La Rosa crude oil. The vertical scale exaggeration is about 45X. The contour for 0.25 ppm was at approximately 9 m at its deepest point; for the 1.0 ppm contour, 4 to 5 m.

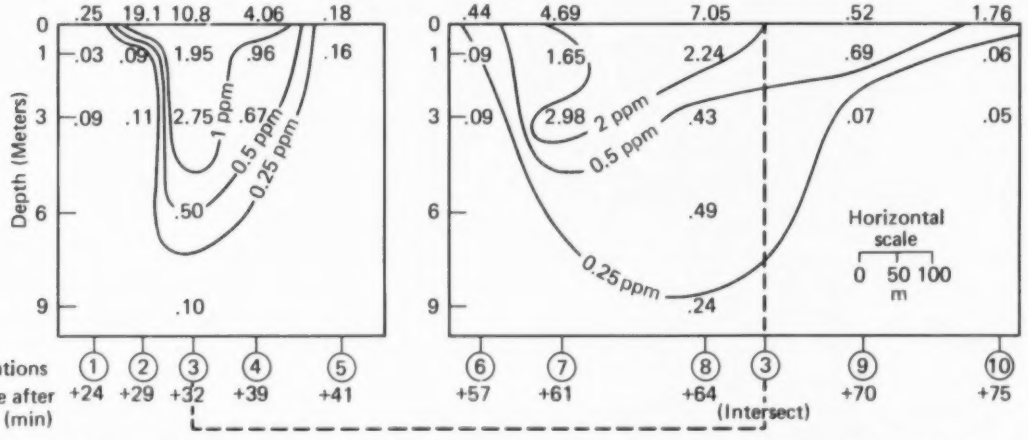

Fig. C-2 Total extractable organic matter (ppm) in water samples collected during first sample run through La Rosa crude oil spill immediately dispersed (oil spilled 1019, dispersed 1028–1035).

The shape of the 2.0 ppm contour on the transect of Stations 6 through 10 is interesting in its asymmetry. Relying as it does on one data point

for its asymmetric shape, this might be suspected as an experimental artifact. However, the second set of transects, approximately 1 hr later (Fig. C-3) produced the same type of contour. Fig. C-3 also shows the lower concentrations brought about by dilution of the plume in a larger volume of water.

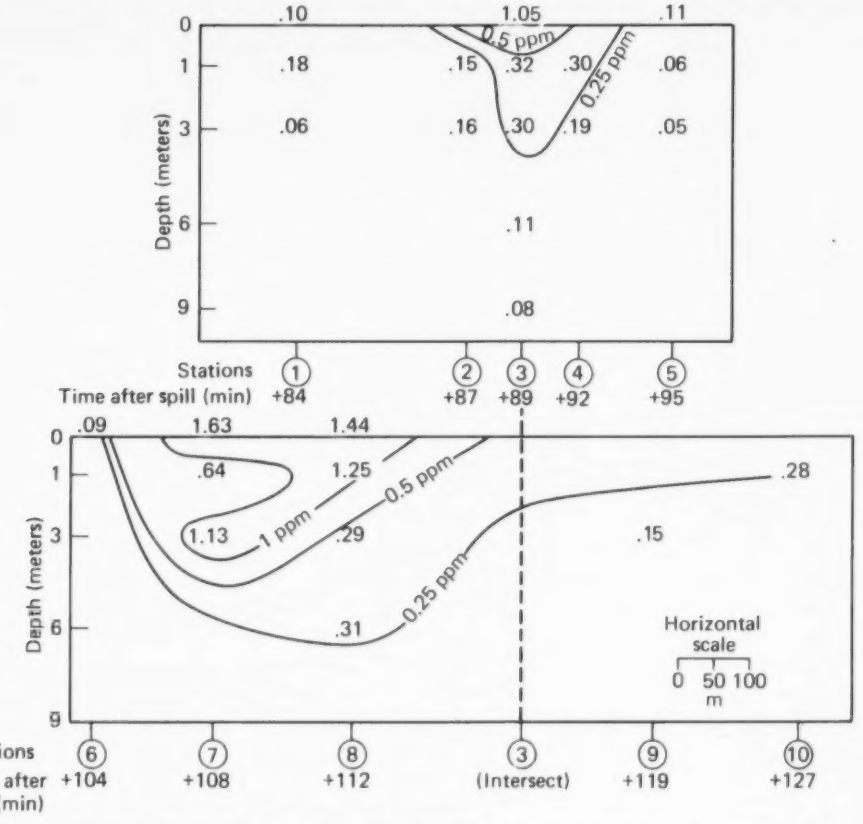

Fig. C-3 Total extractable organic matter in water samples collected during second sample run through La Rosa crude oil spill immediately dispersed.

Petroleum hydrocarbons (C_{14}+) were determined on three of the extracts. Extractable OM was 2.24, 1.25, and 2.54 mg/L; C_{14}+ hydrocarbons were respectively 1.43, 0.72, and 1.97 mg/L. Petroleum hydrocarbons averaged 76% of the total extractable OM. This is in the range previously observed for a much larger number of analyses (Ref. 8). However, the actual crude oil content of the original CCl_4 extracts is higher because hydrocarbons < C_{14} are lost when the CCl_4 is evaporated to 1 mL prior to adding to the top of the silica gel column. Thus, the C_{12} and C_{13} with lesser amounts of C_9 to C_{11} hydrocarbons are present in the original CCl_4 extract. This may amount to 10 to 15%, thereby raising the oil content to 85 to 90%. The percent oil may be even higher for those samples with the highest oil content (>5 ppm).

The polar organic compounds removed by silica gel appear to exceed the extractable OM from background water samples outside the oil spill areas

(particularly noticeable when the extractable OM ranges from 0.2 to 1 ppm). A possible explanation is that crude oil acts as an organic solvent, extracting and concentrating natural organic compounds in sea water.

Another way to view the dilution is shown in Fig. C-4 for the immediately dispersed La Rosa spill. Concentrations at Station 3 in the center of the plume, are plotted with depth over time. Because each depth concentration is a single analysis, great reliance should not be placed on an individual point. As expected, a steady decrease in concentrations toward background values occurred over time.

Concentration lines for the immediately dispersed Murban spill (Fig. C-5) show higher values than with La Rosa (Fig. C-2). Dispersed oil was also found in higher concentrations at greater depths (almost 1 ppm at 9 m).

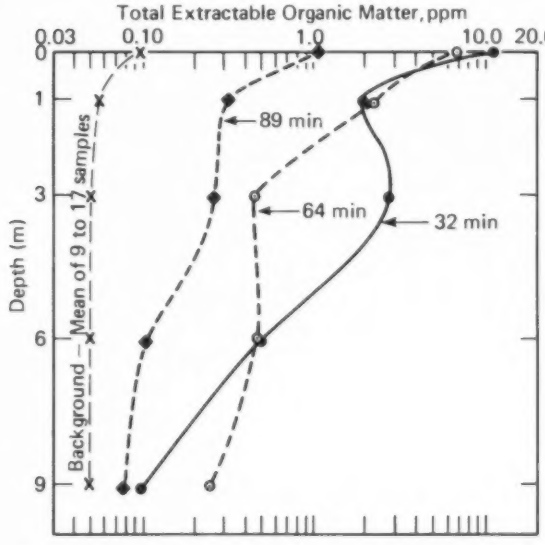

Fig. C-4 Comparison of concentration – depth profiles at one station for various times under the immediately dispersed La Rosa crude oil spill.

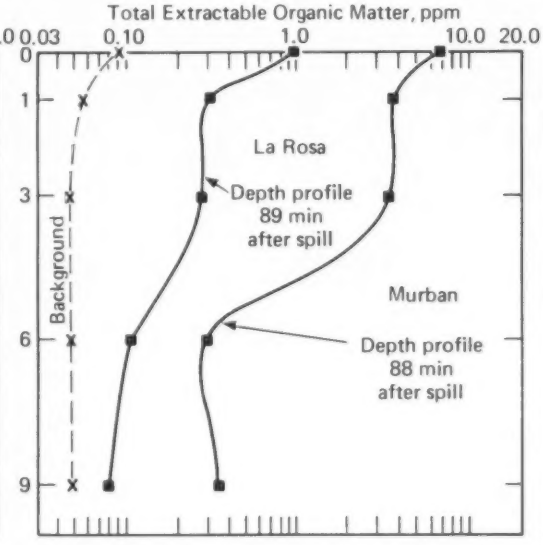

Fig. C-6 Comparison of concentration – depth profiles for La Rosa and Murban crude oils at about the same time following discharge and dispersion.

Fig. C-6 compares concentration-depth profiles of the two crude oils, for samples from the center of the plume at similar times after oil discharge and dispersion. Again, each concentration is a single data point. A rough material balance calculation indicates that the Murban crude oil was almost completely dispersed, whereas the La Rosa was about half dispersed. These evaluations concur with visual impressions of effectiveness.

The data for the two spills that were allowed to weather for 2 hr before dispersion do not allow such clear graphical display. Most values for total extractable OM were much lower than those from the immediately dispersed spills. One explanation is the larger area to be treated after two hours, with a consequently larger water volume available to dilute an

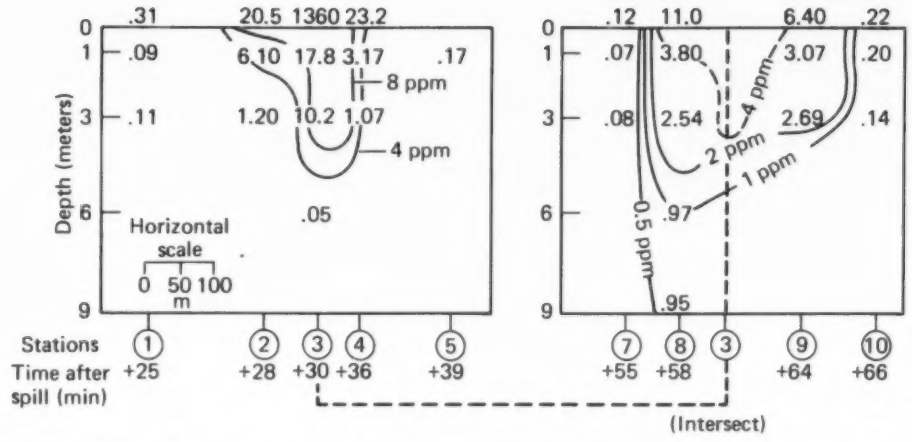

Fig. C-5 Total extractable organic matter (ppm) in water samples collected during first sample run through immediately dispersed Murban crude oil spill (oil spilled 1404, dispersed 1411–1416). The dashed contour for 4 ppm is based on the station 1 to 5 transect.

equivalent amount of oil. Most of the oil was concentrated in the leading (downwind) part of the slick, in perhaps only 10% of the total slick area, as observed by Hollinger and Mennella (Ref. 8). The dispersant was applied uniformly over the whole slick rather than concentrated on the area of heavy oil. Therefore the dispersant to oil application rate was not as high as for the immediately dispersed spills, which were treated before appreciable spreading had occurred. Weathering also would have increased oil viscosities, and thereby would have decreased dispersant effectiveness.

A summary of the total extractable OM in water under the four research oil spills is shown in Table C-2. It includes only values exceeding 0.10 ppm (approximately two times background). Untreated oil dispersed naturally in the water to a lesser extent than chemically treated oil. Immediate dispersion was more effective than after two hours, but most of the difference may be attributed to differences in application rate of dispersant to the oil.

The greatest difference between oils was evident when they were dispersed immediately. Murban oil concentrations were higher at all water depths than for La Rosa. The slightly higher concentrations for La Rosa compared with Murban following delayed dispersion may reflect differences in chemical application and/or sampling locations.

Oil Weathering as Measured by C_1 to C_{10} Analysis

Infrared analysis of CCl_4 extracts provides a measure of total oil in water samples, but is relatively insensitive. It is also complicated by the presence of background hydrocarbons and CCl_4 extractable organic compounds such as acids, alcohols, and esters in sea water. As used in this study, the method had a limit of detection of about 0.02 mg/L. The method also does not give information on individual hydrocarbons, classes of

hydrocarbons, or degree of weathering (loss of low-molecular-weight hydrocarbons).

TABLE C-2 SUMMARY OF CARBON TETRACHLORIDE EXTRACTABLE ORGANIC MATTER IN WATER FROM UNDER FOUR RESEARCH OIL SPILLS (CONCENTRATIONS IN MG/L, PPM)*

	La Rosa			Murban		
	n**	Maximum	Mean	n	Maximum	Mean
Not dispersed						
1 m	4	0.22	0.13	1	0.95	-
3 m	3	.51	.26	2	.16	0.14
Dispersed at 2 hr						
1 m	7	.23	.15	8	.18	.13
3 m	7	1.05	.27	4	.11	.10
6 m	2	.65	.38	1	.14	-
9 m	1	.29	-	1	.12	-
Dispersed within 10 min						
1 m	16	2.24	.69	13	17.80	3.10
3 m	14	2.96	.67	9	10.20	2.45
6 m	5	.50	.31	4	1.00	.45
9 m	1	.25	-	4	.95	.40

*Background concentrations (ppm); 1 m, 0.061; 3 m, 0.050; 6 m, 0.048; 9 m, 0.051
**Number of samples

A gas equilibrium method (Ref. 1, 5) using gas chromatography permits the measurement of most individual hydrocarbons in the C_1 to C_{10} fraction with a limit of detection of 2 ng/L (ppt) for alkanes and cycloalkanes and 10 ppt for aromatic hydrocarbons. This analysis permits the loss of low-molecular-weight hydrocarbons (weathering) to be followed with time (Ref. 1-3).

If adverse biological effects (immediate toxicity) result from oil spills, they are thought to be produced principally by the more soluble low-molecular-weight hydrocarbons (principally aromatics such as benzene and toluene). Of importance, therefore, are the concentrations of the dissolved hydrocarbons and the duration of organism exposure to them. When water is equilibrated with crude oils, the C_1 to C_{10} soluble fraction comprises over 98% of the total soluble hydrocarbons (Ref. 9). For typical crude oils, benzene plus toluene constitute 70 to 80% of the aromatic hydrocarbons, and 62 to 78% of the total C_6+ hydrocarbons (saturates plus aromatics).

Gas Chromatograms. Gas chromatograms of (1) dissolved hydrocarbons in sea water equilibrated with an excess of Murban crude oil from the spill tank; and (2) C_1 to C_{10} hydrocarbons residual in dispersed oil droplets in a water sample collected under the chemically treated Murban oil spill are shown in Fig. C-7.

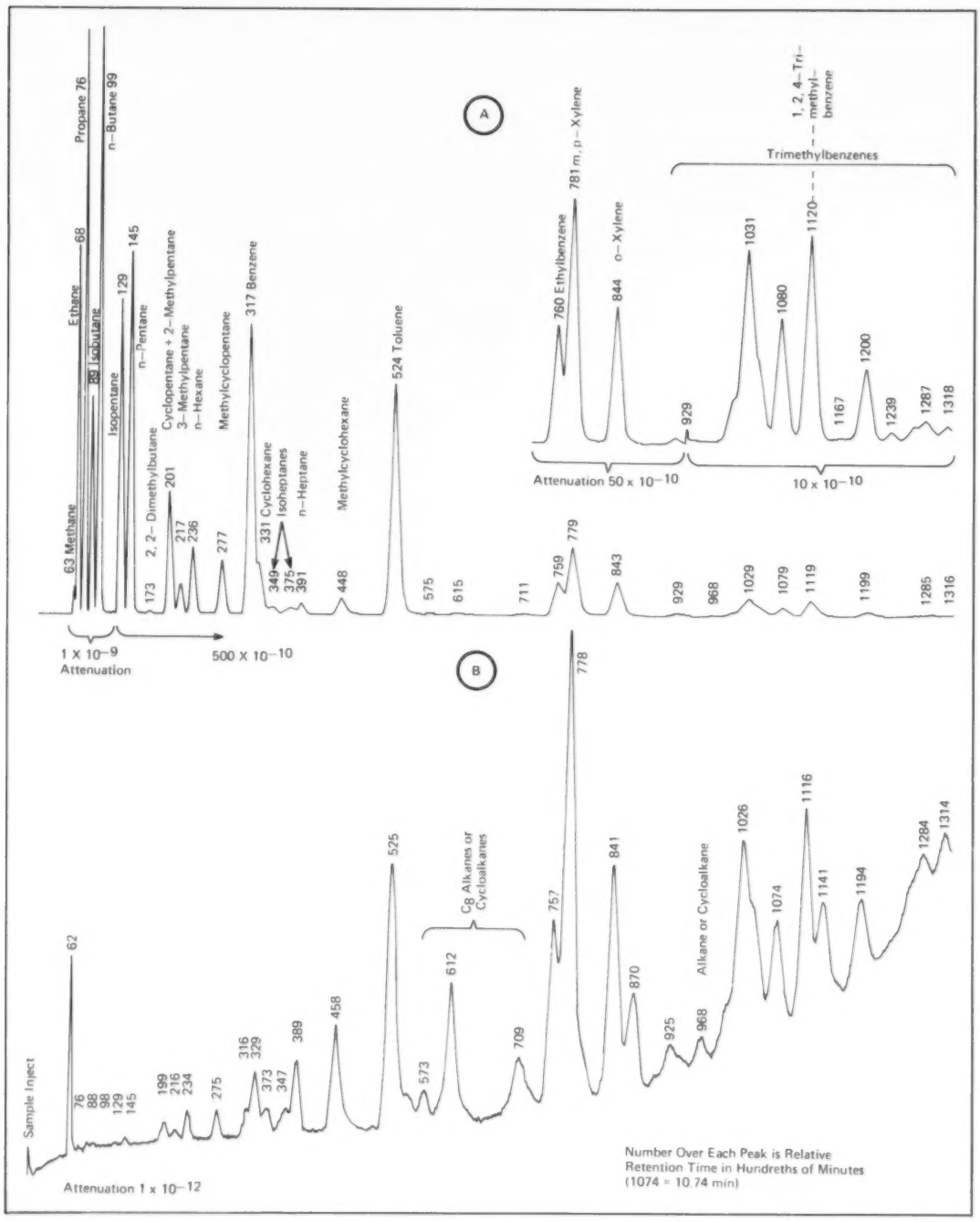

Fig. C–7 Gas Chromatograms: (A) Equilibrium concentrations of dissolved hydrocarbons in sea water mixed with an excess of Murban crude oil from the spill tank. Inset is from second chromatogram with less attenuation to show more clearly the di– and trimethylbenzenes. (B) C_1 to C_{10} hydrocarbons found in 1 m water sample collected 49 min after immediate dispersion of Murban crude oil spill (total extractable organic matter was 3.8 ppm). See text for details of analytical procedures.

The GC column was 6 m of 3.2 mm stainless steel tubing packed with 10% UCW-98 silicone fluid on chromosorb W-HP. The column was temperature programmed from 60° to 145°C at 6°C/min. A 30 cm precut (backflush) column was in a sample valve oven at 100°C. The column was backflushed at 4 min which prevented $>C_{10}$ hydrocarbons from entering the 6 m column. A 2.0 mL (1.6 mm, diameter) sample loop in the sample valve oven introduced 1.5 mL (at 100°C) of the 20 to 23 mL of gas flowed from the 50 mL equilibration syringe through the sample loop.

The numbers over or near the individual hydrocarbon peaks are the relative retention times in hundredths of minutes. Each principal hydrocarbon peak has been named, and the GC amplifier attenuation is given. Fig. C-7A is the gas chromatogram (GC) of dissolved hydrocarbons in sea water equilibrated with Murban crude oil at attenuations of 1×10^9 (methane through pentanes) and 500×10^{10} for the remaining hydrocarbons. The partial GC (Fig. C-7A) is from another analysis with less attenuation, to better show the characteristic di- and trimethylbenzene peaks.

Fig. C-7A shows the marked decrease in concentration of hydrocarbons with increase in molecular weight (carbon number), and the much greater solubility of aromatic hydrocarbons relative to the saturated hydrocarbons of the same carbon number (cycloalkanes are more soluble than alkane hydrocarbons). In particular, note the large benzene and toluene peaks. The decrease is due to not only lower solubility with an increase in carbon number, but also to the lower concentrations of individual hydrocarbons in crude oils (higher carbon numbers than toluene for aromatics) as carbon number increases. An increase in number of isomers occurs with an increase in carbon number.

For pure hydrocarbons, normal alkane solubility decreases six to seven orders of magnitude between carbon numbers 1 and 12. For aromatics, the solubility decreases similarly between carbon numbers 6 and 24 (Ref. 9, 10). For example, hexane, cyclohexane, and benzene, each with six carbon atoms in the molecule, have respective solubilities of 9.5, 60, and 1,750 mg/L (Ref. 10, 11). Thus benzene and cyclohexane are respectively 185 and 6 times more soluble than hexane. The aromatic to n-alkane solubility ratio increases (Ref. 9), so that dimethylnaphthalenes are over 600 times more soluble than n-C_{12}.

Most of the gas was separated from the crude oil. Thus, the peaks in Fig. C-7A for methane through pentanes (particularly methane, ethane, and propane) are lower than if the crude oil was "live" (gas not removed). Figure C-7B represents the C_1 to C_{10} hydrocarbons in a water sample collected at 1 m near the center of the immediately treated Murban spill 46 min after dispersion. The attenuation is 500 times less (1000 times for C_1 to C_5) than in Fig. C-7A, and the peak areas (concentrations) are entirely reversed (methane through the trimethylbenzenes). This qualitatively shows not only the very low concentrations of these low-molecular-weight hydrocarbons (Fig. 7B), but progressively greater loss with decrease in carbon number. Weathering of these low-molecular-weight hydrocarbons was very rapid. Quantitative data are presented in tables that follow.

Weathering of Murban crude oil. Table C-3 shows C_1 to C_{10} hydrocarbons in water samples from 0 to 9 m depths at the center of the Murban slick 46 min after spraying with a self-mix dispersant. The first numerical column "Oil max." gives the equilibrium concentrations of dissolved hydrocarbons in sea water that was thoroughly mixed with an excess of Murban crude oil from the spill tank. Note, as discussed above, the decrease in concentration with increase in carbon number, and the high concentrations of benzene and toluene. The alkane and cycloalkane hydrocarbons (>7 carbon atoms) have become so low that they are difficult to identify and separate from aromatic hydrocarbons (Fig. C-7). Thus n-heptane and methylcyclohexane are the highest carbon number saturate hydrocarbons shown in Table C-3. Methane-through-pentane hydrocarbons (Oil max.) are lower than if the gas had not been separated. In essence, only aromatic hydrocarbons were measured in solution from toluene through trimethylbenzenes. In addition to those peaks designated as alkane or cycloalkane (Fig. C-7b), peaks 870 and 1141 are also nonaromatic (compare Fig. C-7A and C-7B). These peaks arise from presence of nondispersed oil and presumably droplets smaller than the filter used to remove most of the separate phase oil.

The concentrations of the individual hydrocarbons found in the dispersed (emulsion) plume of the Murban crude oil confirm the distribution and values indicated in Fig. C-7B. They are very low, and the lowest carbon numbers are present in the lowest concentrations. This is the opposite of that expected if solution were an important process.

Consider the hypothetical situation of oil on a water surface with (1) evaporation prevented, and (2) a limited volume of water maintained in contact with the oil (i.e., the laboratory conditions for mixing a sample of crude oil from the spill tank with sea water in a sealed glass bottle). Under equilibrium conditions, one would expect to find the concentrations and relative concentrations as shown in Oil max., Table C-3. Removing the restriction on water movement, but preventing evaporative loss would result in nonequilibrium solution of hydrocarbons into the water, and the rate of solution of individual hydrocarbons would become important (just as for evaporation).

The rate of solution increases with decrease in carbon number, and with class of hydrocarbon (i.e., aromatic vs alkane for the same carbon number). Under nonequilibrium conditions, methane would go into solution faster than ethane, ethane faster than propane, etc. Similarly, benzene would go into solution faster than toluene, toluene faster than xylenes, etc.

The concentration of each hydrocarbon becomes progressively lower as the degree of departure from equilibrium increases. Thus, the shorter the contact time of oil and water, the lower the concentration of each hydrocarbon in water, and the higher the relative concentrations for those hydrocarbons having the lowest carbon numbers for each class of hydrocarbons (alkane, cycloalkane, and aromatic). Because this was not observed in the water samples under the slick, leads to the conclusion that solution is apparently not a very important process, even when crude oil is chemically dispersed and emulsion droplets penetrate the water column.

TABLE C-3 LOW-MOLECULAR-WEIGHT HYDROCARBONS IN WATER SAMPLES FROM VARIOUS DEPTHS COLLECTED 45 MIN AFTER IMMEDIATE DISPERSION OF MURBAN CRUDE OIL

Depth, m		0		1		3	6	9
Extractable OM, mg/L		11.0		3.8		2.54	0.97	0.95
Hydrocarbons, µg/L (Oil max.)*								
Methane	102	.077		.070		.072	.070	.073
Ethane	1560	.004	.0003**	.002	.0001	-	-	-
Propane	2360	.009	.0004	.004	.0002	-	-	-
Isobutane	940	.006	.0006	.003	.0003	-	-	-
n-Butane	2720	.004	.0002	.002	.0001	-	-	-
Isopentane	870	.002	.0002	.002	.0002	-	-	-
n-Pentane	1080	.007	.0006	.005	.0005	-	-	-
Cyclopentane	510	.026	.005	.012	.002	-	-	-
3-Methylpentane	125	.023	.018	.006	.005	-	-	-
n-Hexane	290	.072	.025	.022	.008	-	-	-
Methylcyclopentane	280	.092	.033	.027	.010	-	-	-
Benzene	6080	.260	.004	.095	.002	.041	.041	-
Cyclohexane	270	.205	.076	.066	.024	.011	.018	-
n-Heptane	65	.34	.52	.067	.103	.008	.020	-
Methylcyclohexane	140	.59	.42	.135	.096	.040	.022	-
Toluene	5630	3.75	.067	1.40	.025	.395	.48	.26
Ethylbenzene	610	2.25	.37	.80	.13	.285	.23	.075
m, p-Xylene	1550	7.70	.50	2.55	.16	1.05	.95	.50
o-Xylene	900	5.45	.61	1.85	.21	.75	.57	.24
926*** Trimethylbenzene	68	.42	.62	.12	.18	.050	.035	.023
1027 Trimethylbenzene	800	6.50	.81	1.55	.19	.74	.50	.27
1077 Trimethylbenzene	370	2.75	.74	.65	.18	.30	.16	.035
1,2,4-Trimethylbenzene	920	6.20	.67	1.40	.15	.75	.31	.065
1197 Trimethylbenzene	300	3.20	1.07	.66	.22	.38	.13	.040
Total saturates	11,300	1.46		.42		.13	.13	.07
Total aromatics	17,200	38.5		11.1		4.75	3.41	1.51
Total hydrocarbons	28,500	40		11.5		4.90	3.54	1.58

*Equilibrium concentrations of dissolved hydrocarbons when an excess of Murban crude oil from the spill tank was mixed with sea water
**Underscored value is percent hydrocarbon found in water sample compared with equilibrium concentration of dissolved hydrocarbon (Oil max.)
***Number is relative retention time (see Fig. C-7)

It appears that evaporation is the dominant process. The low-molecular-weight hydrocarbons that do dissolve apparently quickly evaporate to the atmosphere or dilute to very low concentrations. The hydrocarbons in solution measured in the water samples (Table C-3) apparently were not in true solution at the time of collection, but residual in separate-phase oil droplets. After collection, they equilibrated between the oil droplets and water. The equilibrium solubility of C_{10}^{+} hydrocarbons in crude oils is

very low, probably less than 10 ppb. Thus, the separate oil phase in the samples ranged from about 11,000 ppb in the surface sample to 940 ppb in the 9 m sample, 300 to 600 times the total dissolved hydrocarbon concentrations.

The data in Table C-3 show that the residual hydrocarbons are low in concentration, even for the surface-collected sample. Thus, the biologically toxic low-molecular-weight hydrocarbons have been quickly lost. The concentration of the least volatile, trimethylbenzene (1197), is only 1.07% of the equilibrium solubility for unweathered oil (Oil max.). The remaining percentages (Column 3) show a generally progressive decrease with carbon number (0.0002 to 0.0006% for ethane through pentane hydrocarbons).

The percentages found at 1 m (Column 5) are even lower, showing that oil emulsion at this depth is more weathered than oil droplets at the surface. Accelerated weathering is noted with increasing depths as shown by decreasing concentrations and by percentages if calculated for 3, 6 and 9 m. For example, 1,2,4-trimethylbenzene concentrations in the dispersed oil droplets for 0, 1, 3, 6, and 9 m are respectively 0.67, 0.15, 0.08, 0.03, and 0.007%.

Because the samples were collected simultaneously, the accelerated weathering with increasing depth apparently relates to smaller droplet sizes. Evaporation and solution are diffusion processes; and the shorter the diffusion pathway, the higher the rate. As droplet size decreases, the surface-to-volume ratio increases, with resulting faster loss of volatile and soluble hydrocarbons.

It seems reasonable to expect smaller droplets at greater depth. Oil-in-water emulsions have a size distribution that ranges from 0.1 to 100 mm (Ref. 12). The larger droplets (some may be even larger than 100 mm, Ref. 13) will be buoyant (Murban crude oil has a specific gravity of 0.83), and will rise toward the water surface after mixing downward by wave action. However, below diameters of about 2-3 mm, gravitational effects are balanced by Brownian forces. These small droplets move by Brownian motion and will disperse in all directions, just as clay-sized (< 2 mm) mineral particles stay indefinitely suspended in water.

The percents for the aromatics benzene and toluene in Column 3, Table C-3 are 0.004 and 0.067 whereas methylcyclopentane, cyclohexane, n-heptane, and methylcyclohexane are 0.033, 0.076, 0.52, and 0.42 respectively. Thus benzene and toluene are very much lower. This is also shown to a lesser extent for the percents of these hydrocarbons in Column 5. This also suggests that the hydrocarbons found in waters associated with the dispersed slick were residual in the droplets and not in true solution at the time of collection. These data indicate that benzene and toluene were lost more rapidly by solution (although evaporation greatly predominates) than the corresponding carbon-number-saturates; and that once lost, were subsequently evaporated or quickly diluted. Had these aromatics been in true solution at time of collection, their concentrations should have been higher than the corresponding-carbon-number alkane and cycloalkane hydrocarbons.

The concentration of methane (Table C-3) is constant at about 70 ppt. This reflects the expected equilibrium concentration of methane in sea water with that in the atmosphere for this region of the Atlantic Ocean (Ref. 14).

Table C-4 presents the concentrations of C_1 to C_{10} hydrocarbons in water samples collected at 1 m over the time (18 to 110 min) that measurable oil could be detected. These data show the rapid loss of volatile hydrocarbons with time. Even at 18 min, the trimethylbenzenes average a little over 1% remaining in the dispersed oil droplets. This 18 min sample had the highest observed oil content (17.8 ppm) of all the subsurface samples collected.

TABLE C-4 LOW-MOLECULAR-WEIGHT HYDROCARBONS IN WATER SAMPLES COLLECTED OVER INCREASING TIME AT 1 MM UNDER THE IMMEDIATELY DISPERSED MURBAN CRUDE OIL SPILL

Time after dispersion, min		18	46	72	110
Extractable OM, mg/L		17.8	3.8	1.55	0.31
Hydrocarbons, g/L					
Ethane	.004	.0003*	.002	-	-
Propane	.016	.0007	.004	-	-
Isobutane	.008	.0008	.003	-	-
n-Butane	.006	.0002	.002	-	-
Isopentane	.003	.0003	.002	-	.008
n-Pentane	.007	.0006	.005	-	.006
Cyclopentane	.004	.0008	.012	-	.004
3-Methylpentane	.010	.008	.006	.008	.008
n-Hexane	.024	.008	.022	.006	.008
Methylcyclopentane	.036	.013	.027	.018	.006
Benzene	.117	.002	.095	.020	.024
Cyclohexane	.139	.051	.066	.041	.040
n-Heptane	.128	.196	.067	-	-
Methylcyclohexane	.315	.225	.135	.014	-
Toluene	3.50	.062	1.40	.55	.150
Ethylbenzene	2.20	.360	.80	.42	.090
m, p-Xylene	8.85	.57	2.55	1.80	.429
o-Xylene	5.65	.63	1.85	1.13	.300
926 Trimethylbenzene	.50	.73	.12	.07	.029
1027 Trimethylbenzene	8.95	1.12	1.55	1.06	.051
1077 Trimethylbenzene	3.90	1.05	.65	.51	.078
1,2,4-Trimethylbenzene	7.52	.82	1.40	1.13	.175
1197 Trimethylbenzene	4.60	1.53	.66	.68	.120
Total saturates	.70		.35	.09	.08
Total aromatics	45.8		11.1	7.4	1.45
Total hydrocarbons	46.5		11.5	7.5	1.53

*Underscored value is percent hydrocarbon found in water sample compared with equilibrium concentration of dissolved hydrocarbon (Table 3, Oil max.)

The decreasing percentage with decrease in carbon number (Column 3) confirms data in Table C-3 showing that these measured hydrocarbons are

residual in the emulsion droplets. Note again that solution preferentially removed benzene and toluene (and probably the higher aromatic hydrocarbons, but to a lesser extent) from these droplets compared with corresponding carbon number saturates.

Weathering of La Rosa crude oil. Table C-5, for immediately dispersed La Rosa crude oil, shows the concentrations of low-molecular-weight hydrocarbons in water samples collected at 0 and 3 m, and 47 and 94 min after dispersion. Also shown are the equilibrium concentrations of dissolved hydrocarbons attainable when an excess of La Rosa crude oil was thoroughly mixed with sea water (Column 1, Oil max.), and the percent of hydrocarbons remaining in the dispersed droplets (Columns 4 and 7).

The equilibrium concentrations (Oil max) for La Rosa are somewhat different from Murban, reflecting the differences in specific gravities and viscosities. La Rosa has less C_5+ hydrocarbons than Murban, but comparable C_1 to C_4. The lower C_5+ concentrations reflect the lower naphtha fraction (La Rosa, 11 volume %; Murban, 19%, Ref. 2). The comparable C_1 to C_4 concentrations are probably related to less complete separation of gas from the more viscous La Rosa.

The hydrocarbons in water samples also reflect the apparently slower diffusion (evaporation and solution) from the more viscous La Rosa crude oil, particularly for the C_1 to C_4 fraction. There also was a slower change in concentration with time and depth, compared with Murban.

This slower weathering may be due not only to higher viscosity, but also to larger droplet sizes. Observations and extractable oil reported previously show La Rosa to have been less effectively dispersed, compared with the almost complete dispersion of Murban. However, the generally lower concentrations were more uniformly dispersed to 6 m (Table C-2). The larger La Rosa droplets being less buoyant may well have mixed downward by wave action more easily than Murban.

Although the weathering of La Rosa was slower, it should also be noted that the concentrations of low-molecular-weight hydrocarbons were very low in the water samples. The highest concentrations of an individual hydrocarbon was 1.5 ppb toluene at 3 m, 47 min after dispersion; and 0.6 ppb at 3 m, 94 min after dispersion. Total low-molecular-weight hydrocarbons were less than 15 ppb for all samples.

The percent benzene and toluene (Columns 4 and 7) show as for Murban crude oil, that these aromatics were preferentially removed by solution from the oil droplets. However, once removed, they apparently very quickly diluted or evaporated to the atmosphere, as previously discussed.

SUMMARY AND CONCLUSIONS

Four research oil spills (1.7 m3 each) of two crude oils (Murban, 0.83 specific gravity; and La Rosa, 0.91) were made 40 km off New Jersey. Two spills were immediately sprayed by helicopter with a self-mix dispersant; two, after 2 hr.

TABLE C-5 LOW-MOLECULAR-WEIGHT HYDROCARBONS IN WATER SAMPLES COLLECTED AT TWO DEPTHS AND AT TWO TIMES FOLLOWING IMMEDIATE DISPERSION OF LA ROSA CRUDE OIL

Depth, m		0	3		0	3	
Time after dispersion, min		47	47		94	94	
Extractable OM, mg/L		4.70	2.96		1.63	1.13	
Hydrocarbons, g/L	(Oil Max.)*						
Methane	170	.073	.053		.077	.076	
Ethane	1740	.070	.083	.005**	.064	.045	.003
Propane	2360	.38	.36	.015	.30	.19	.008
Isobutane	620	.25	.25	.040	.20	.12	.019
n-Butane	1510	.57	.59	.039	.48	.26	.017
Isopentane	470	.47	.53	.113	.38	.21	.045
n-Pentane	480	.35	.45	.094	.33	.17	.035
Cyclopentane	330	.43	.52	.16	.34	.17	.051
3-Methylpentane	72	.13	.18	.25	.12	.05	.069
n-Hexane	125	.13	.23	.18	.17	.07	.056
Methylcyclopentane	230	.46	.57	.25	.34	.18	.078
Benzene	2870	.60	.50	.017	.37	.20	.007
Cyclohexane	270	.63	.76	.28	.37	.19	.070
n-Heptane	23	.09	.09	.39	.07	.03	.13
Methylcyclohexane	120	.49	.51	.43	.36	.17	.14
Toluene	2370	1.80	1.50	.063	1.10	.57	.024
Ethylbenzene	300	.66	.59	.20	.41	.20	.067
m, p-Xylene	680	1.75	1.40	.21	1.05	.51	.075
o-Xylene	360	1.30	1.05	.29	.77	.40	.110
926 Trimethylbenzene	24	.15	.14	.58	.08	.04	.17
1027 Trimethylbenzene	170	.94	.66	.39	.61	.43	.25
1077 Trimethylbenzene	55	.35	.20	.36	.18	.10	.18
1,2,4-Trimethylbenzene	125	1.15	.65	.52	.67	.34	.27
1197 Trimethylbenzene	75	.90	.47	.63	.51	.27	.36
Total saturates	8520	4.52	5.18		3.60	1.93	
Total aromatics	7030	9.60	7.16		5.75	3.06	
Total Hydrocarbons	15,500	14.1	12.3		9.3	5.0	

*Equilibrium concentrations of dissolved hydrocarbons when an excess of La Rosa crude oil from the spill tank was mixed with sea water

**Underscored value is percent hydrocarbon found in water sample compared with equilibrium concentration of dissolved hydrocarbon (Oil max.)

Water samples were collected over time at 1, 3, 6, and 9 m under the nontreated slicks and following dispersion. The dispersant application and the sampling were directed from another aircraft. This plane also provided a platform for observation of dispersant effectiveness and taking of color photographs.

Water samples were analyzed by IR for total oil content of a carbon

tetrachloride extract; and for weathering of the C_1 to C_{10} hydrocarbon fraction, by gas chromatography.

Total oil under the immediately dispersed slicks at 1, 3, 6, and 9 m were respectively: La Rosa - 0.7, 0.7, 0.3 and 0.2 mg/L; Murban - 3.1, 2.4, 0.5, and 0.4 mg/L. The highest concentrations (30 to 90 min after dispersion) were La Rosa, 3 mg/L; Murban, 18 mg/L.

Oil concentrations for dispersion delayed 2 hr were lower ($\leq$ 1.1 mg/L), and only slightly higher than found under nondispersed oil (highest concentration for La Rosa was 0.5 mg/L; for Murban, 0.9. The less effective dispersion after delayed treatment reflects lower and less efficient dispersant application for these small spills, as well as increased oil viscosities due to weathering.

Samples collected 2 to 4 hr after dispersion contained no more than 2 to 3 times background concentrations of about 0.06 mg/L.

Rough material balance calculations, supported by visual and photographic evidence, indicate that Murban crude oil treated immediately was almost completely dispersed; for La Rosa, about half was dispersed. It follows that oil removed from the influence of wind will not travel as far, and thereby reduce the likelihood of oil stranding or entering biologically sensitive areas.

The dispersed oil in the water column weathered very rapidly. Evaporation of C_1 to C_{10} hydrocarbons greatly exceeded solution. Relative concentrations of the individual C_1 to C_{10} hydrocarbons show that dissolved hydrocarbons (including benzene and toluene) were not present at $<$ 0.01 µg/L detection limit. Apparently the more soluble hydrocarbons quickly evaporate or dilute to even lower concentrations.

The measured C_1 to C_{10} hydrocarbons were residual in dispersed oil droplets, and did not exceed 50 µg/L, even for samples collected at 1 m and 18 min after dispersion. After 2 hr this had decreased to $<$ 2 µg/L.

Weathering increased from the surface to 9 m depth for samples collected at the same time, indicating decreasing droplet sizes with increasing depth. Weathering also increased with time for samples collected at the same depth.

Murban crude oil dispersions weathered more rapidly than La Rosa, reflecting Murban's lower viscosity (and possibly smaller droplet sizes).

The rapid weathering of low-molecular weight hydrocarbons from dispersed crude oil droplets should quickly reduce biological toxicity from hydrocarbons such as benzene and toluene.

The observed changes in concentrations and weathering of chemically-dispersed crude oils provide real-world data that can assist in the design of initial concentrations and dilutions for realistic laboratory bioassays.

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